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EVALUATION OF INSTRUMENTATION FOR MONITORING TOTAL MERCURY EMISSIONS FROM STATIONARY SOURCES

ABCOR, INCORPORATED

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NATIONAL ENVIRONMENTAL RESEARCH CENTER

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16. ABSTRACT

The principal objective of this project was to identify and evaluate monitoring instrumentation which represents the current state-of-the-art in measurement of total mercury emissions from stationary sources. During the laboratory test program the uniformity of response of each instrument acquired for the program to expected forms of mercury emissions from stationary sources including particulate and organomercury compounds as well as elemental mercury vapor was established. Field tests were conducted at the following sources: (1) secondary processing of mercury; (2) chloralkali production; and (3) nonferrous (zinc) smelting. From the evaluation of these data the investigators concluded that available mercury measuring instrumentation can be adapted for the measurement of total mercury emissions from certain sources, in particular, chlor-alkali plants. The transporting and conditioning of the sample poses considerable difficulties requiring additional research. The necessity of a dynamic dilution system to condition high level mercury emissions sets the requirement for a fairly sophisticated automatic interfacing subsystem. Manual control was accomplished during the field and laboratory portions of the program. Manual control in the field was sufficient for these studies; however, continuous monitoring could not be accomplished by this means.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Mercury Source Monitors	Mercury Source Emissions Monitors for mercury compounds.	

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I. INTRODUCTION

A. BACKGROUND

This program was initiated in July 1972. The principal objective was to identify and evaluate monitoring instrumentation which represents the current state-of-the-art in the measurement of total mercury emissions from stationary sources. The requirements for continuous mercury monitors are set principally by the characteristics of the emission sources to which they are applied. Since emissions from these sources are of different chemical and physical compositions, the choice of and operations of the several monitors and sampling system had to be varied.

The program was initially scheduled for nine months, including a three month field program conducted at the following three mercury sources: (1) chlor-alkali production; (2) primary processing of mercury; and (3) secondary recovery of mercury. The field test program was to be preceded by a two-month laboratory test program. During this phase, the uniformity of response of each instrument acquired for the program to all expected forms of mercury emissions from stationary sources including particulate and organomercury compounds as well as elemental mercury vapor would be established.

The following data was to be obtained on each instrument during the lab and field tests:

a. accuracy
b. precision
c. sensitivity
d. stability
e. response time
f. interferences
g. reliability
h. response to different mercury species
i. sample treatment required

Finally, all data obtained in the laboratory and field tests was to be evaluated and recommendations made in the following areas: (1) standard procedure for use of recommended instruments; (2) performance specifications for a total mercury monitor in given application; and (3) recommendations for future research and development programs to correct deficiencies in existing instruments.

A four-month extension was granted due to delays in receipt of certain equipment and delays attendant upon the change in Program Director, extending the completion date to July 28, 1973. Also, the "Scope of Work" was modified by altering the three mercury sources for the field test program to be as follows: (1) secondary processing of mercury; (2) chlor-alkali production; and (3) nonferrous (zinc) smelting. This change reflected the relative importance of nonferrous smelting since primary processing of mercury has virtually disappeared as a source of mercury in the United States.

B. SUMMARY

It was found that available mercury measuring instrumentation can be adapted for the measurement of total mercury emissions from certain stationary sources, in particular, chlor-alkali plants. The transporting and conditioning of the sample poses considerable difficulties requiring additional research. The necessity of a dynamic dilution system to condition high level mercury emissions sets the requirement for a fairly sophisticated automatic interfacing subsystem. Manual control was accomplished during the field and laboratory portions of the program. Manual control in the field was sufficient for our studies, however, continuous monitoring could not be accomplished by this means.

The two-wavelength instruments evaluated in this program, i.e., Dupont and Olin units appeared to be amenable to applications as continuous monitors. The single-beam instruments evaluated in this program were not designed for continuous monitoring although the Beckman unit performed adequately to be employed as a portable analyzer. Again, the problem of system interfacing would limit the instruments applicability. The inherent very high sensitivity of the Geomet unit would require either analyzer modifications or an extremely delicate interface system in order to use it or similar instruments in a continuous monitoring system. The Sunshine monitor and the tape stain sampler did not perform satisfactorily to be considered as adaptable for monitoring use.

II. MERCURY EMISSIONS AND INSTRUMENTATION

A. BRIEF DESCRIPTION OF MERCURY EMISSIONS

The principal sources of mercury in the atmosphere include:

a. chlor-alkali production

b. primary mercury production

c. secondary mercury production

d. non-ferrous smelting

e. coal burning power plants

f. incinerators

g. organic mercurial products decomposition

h. laboratories and hospitals

The latter two sources are not stationary sources in the conventional sense; however, the others represent potential stationary sources. Although the EPA emission standards for mercury (40 CFR 61:38 FR8820, April 6 , 1973) were applicable only to those stationary sources which process mercury ore to recover mercury and mercury chlor-alkali production, other sources listed above emit mercury at significant levels.

Data from the background document on mercury standards (EPA, 1971) indicates that total mercury emissions from 31 chlor-alkali plants in the U.S. in 1969 (uncontrolled) was about 300 tons per year. Uncontrolled emissions from primary mercury producers are estimated to amount to 2 to 3% of the mercury recovered or about 20 to 25 tons per year. However, no primary mercury facilities are presently in operation. Emissions figures from secondary processing of mercury are not available, but it seems reasonable that unit losses will be in the same range as those for primary sources. Thus, secondary losses should be of the order of 20 to 25 tons per year.

Coal contains mercury in amounts ranging from less than 0.05 ppm to around 0.5 ppm. The utility coal consumption (306,000,000 tons) from 1969 data (NCA, 1970) and a representative Illinois coal (0.18 ppm), yield a calculated value of mercury emitted from coal-fired boilers nationally of about 50 to 60 tons per year.

Estimates of emissions from the other two large sources, incinerators and non-ferrous smelters are more difficult to determine.

The first three of the sources listed above not only are important from a total emission basis, but also may release emissions at high concentrations (100 milligram per cubic meter and higher). Non-ferrous smelters also may release emissions of high concentrations. This data indicates that instruments with high ranges of mercury concentrations would be preferable; however, no monitoring instruments were found available that responded at this high a level. The alternative method developed in this program was a dilution system capable of reducing high mercury concentrations to those levels of the instruments.

B. INSTRUMENT SUMMARY

1. General Summary

Mercury has very strong absorption at 253.7 nm, the mercury resonance line, with an extinction coefficient of approximately 5×10^6. This absorption is one hundred to one hundred thousand times higher than that of other species. Thus, if a mercury lamp is used as a light source, the detection of mercury is quite sensitive and selective. All but one of the mercury monitors employed in this contract was based on this technique of ultraviolet absorption.

The remaining monitor was a tape-stain sampler operating on the principle that free mercury reacts with selenium sulfide-coated paper to produce black HgS. The decrease in the percent transmittance of the paper is directly proportional to the mercury concentration. Radiochemical detection, neutron activation analysis, and flameless atomic absorption spectroscopy, which are used routinely in the laboratory are not considered monitoring equipment and are not included.

The monitors relying on the technique of ultraviolet detection (absorption) of elemental mercury at 253.7 nm must be treated so that the mercury vapor is free of interferences and all particulate mercury converted to elemental mercury. The major interferences would be from organic (aromatic) compounds which have high extinction coefficients ($\epsilon \sim$ 10-20,000 ℓ/mole-cm) and sulfur dioxide which has a low extinction coefficient but occurs in high concentrations at smelters. A pyrolyzer operating at a temperature of 600°C was employed to convert all organic compounds to carbon dioxide and water vapor, and a sodium carbonate scrubbing solution was used to selectively absorb sulfur dioxide. The pyrolyzer also converted all organic and inorganic mercury compounds to elemental mercury.

The Olin and Dupont are dual-wavelength instruments capable of minimizing or eliminating the effects of interfering materials in the sample stream. The Beckman and Sunshine are single-beam instruments, electronically less sophisticated than the Olin and Dupont, and are unable to minimize or eliminate any effects of interfering materials in the sample stream. The Geomet is also a single-beam instrument, yet removes interferences through the consecutive heating of two silver grids.

The majority of mercury monitors available are based on the technique of UV absorption. It is for this reason that most of the instruments studied in this program were based on this principle of operation. However, there are other methods of measurement that warrant a description of their principles of operation.

Correlation spectroscopy is a special technique which can be applied to UV absorption spectroscopy. A high resolution mask of the absorption spectrum of mercury is vibrated in and out of the beam and the signal is detected with an AC amplifier (phase-sensitive detector). The advantage of this technique is that interferences from hydrocarbons and sulfur dioxide are eliminated. The major drawback is that the cost of the instrument is prohibitive (approximately twenty thousand dollars). An example of an instrument that employs this technique is manufactured by Barringer Research Corporation.

A commercially available analyzer for measuring elemental mercury vapor by means of condensation nuclei formation has been introduced by Environment/One Corporation. A .1-100 liter sample is drawn through a silver wool cartridge and heated. The mercury is then passed over a mercury ultraviolet lamp to cause formation of mercuric oxide particulates. This air stream is humidified and drawn into a vacuum chamber where constant volume expansion produces a cloud. The transmission of the cloud is related to the concentration of mercury. This instrument was not included in this program due to its high cost and applicability to only extremely low level concentrations of mercury. The Scintrex 1 analyzer employs a pulsed magnetic field applied to a mercury lamp source to obtain pulsed Zeeman components used as reference wavelengths. The elemental vapor concentration is measured as the difference between the absorptions at the 253.7 nm line and at the Zeeman components.

The choice of instruments for use in the program was made to provide a typical array of commercially available and moderate cost instruments. The Beckman was chosen as a single-beam instrument reportedly to be of high quality. The Sunshine was chosen as a second single beam instrument with no knowledge of its past performance. The Olin and Dupont were included as dual-wavelength instruments, based on their present use throughout industry. The Geomet was included as a single-beam instrument capable of removing interferences through the application of silver grids. Finally, the RAC Tape Stain Sampler was included to determine whether it had possible applications in the continuous monitoring field.

2. Beckman K-23A Mercury Vapor Meter

The Beckman Model K-23A Mercury Vapor Meter (Figure 2-1) is a small, portable, ultraviolet photometer. It is set for a wavelength of 253.7 nanometers, and with its two meter scales, reads a full range of 0-1.0 milligram of mercury per cubic meter of air. The meter is used to determine the vapor concentration of mercury in air. However, the instrument used in this study was adapted for monitoring gas samples by inserting an 8 3/4" aluminum cell with fused quartz windows to transport the sample through the analytical beam. Also, the Beckman K-23A was designed for intermittent checking of mercury vapor levels and was not specifically designed for continuous monitoring.

A mercury vapor lamp emits ultraviolet energy with a wavelength of 253.7 nanometers. A mercury vapor sample absorbs energy of the same wavelength while passing through the cell. The mercury vapor lamp is used as a source for both the analytical and reference beams. The analytical beam runs through the cell and passes through a single ultraviolet filter before it falls on the analytical phototube. The reference beam is enclosed and is shorter than the analytical beam extending across the width of the instrument. It passes through a screen attenuator, an adjusting aperture, a fixed aperture and an ultraviolet filter before falling on the reference phototube. The operating principle is diagrammed in Figure 2-2.

3. Dupont 400 Photometric Analyzer

The Dupont 400 Photometric Analyzer (Figure 2-3) provides a means to continuously analyze, on stream, a variety of liquids and gases. Various configurations of optical filters and light sources provide selectivity for liquids or gases which absorb ultraviolet or visible light in the 210 to 1,000 nanometers range. In the analyzer, the light beam is split into a measuring beam and a reference beam after passing through the sample. The analyzer used in this program was provided with optical filters selective for the measurement of mercury.

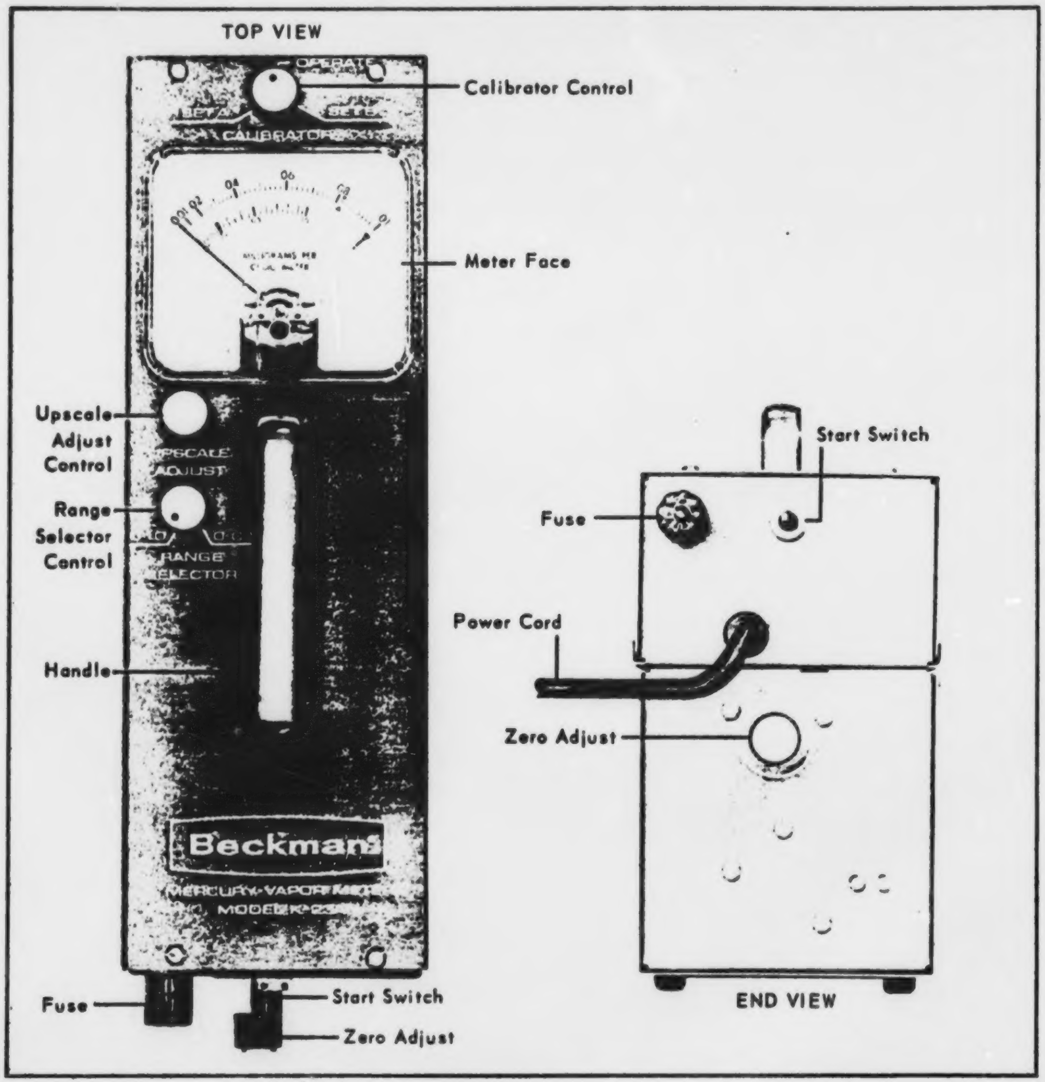

TOP VIEW
OPERATE
SET A
SET B
CALIBRATOR
Calibrator Control
Meter Face
Upscale Adjust Control
UPSCALE ADJUST
Range Selector Control
RANGE SELECTOR
Handle
Beckman
MERCURY VAPOR METER
MODEL K-23A
Fuse
Start Switch
Zero Adjust
Start Switch
Fuse
Power Cord
Zero Adjust
END VIEW

Figure 1. Controls of Model K-23A Mercury Vapor Meter

CONTROL	FUNCTION
START SWITCH	Double-action pushbutton switch. Activates power to instrument.
UPSCALE ADJUST	Sensitivity control. Used to set span sensitivity when calibrating instrument.
RANGE SELECTOR	Used to select 0 to 0.1 or 0 to 1.0 range on the meter.
CALIBRATOR	Three-position switch. SET A is used in calibration of 0 to 0.1 range, SET B for calibration of 0 to 1.0 range, and OPERATE for taking test readings.
METER FACE	The meter has two scales. The top scale is used to read the 0 to 0.1 mg/cubic meter range of mercury contamination. The bottom scale is used to read the 0 to 1.0 mg/cubic meter range of mercury contamination.
ZERO ADJUST	Used to balance the optical zero. Clockwise rotation of the ZERO ADJUST must cause the meter needle to move upscale.

Figure 2-1. Beckman Mercury Vapor Meter, Model K-23A

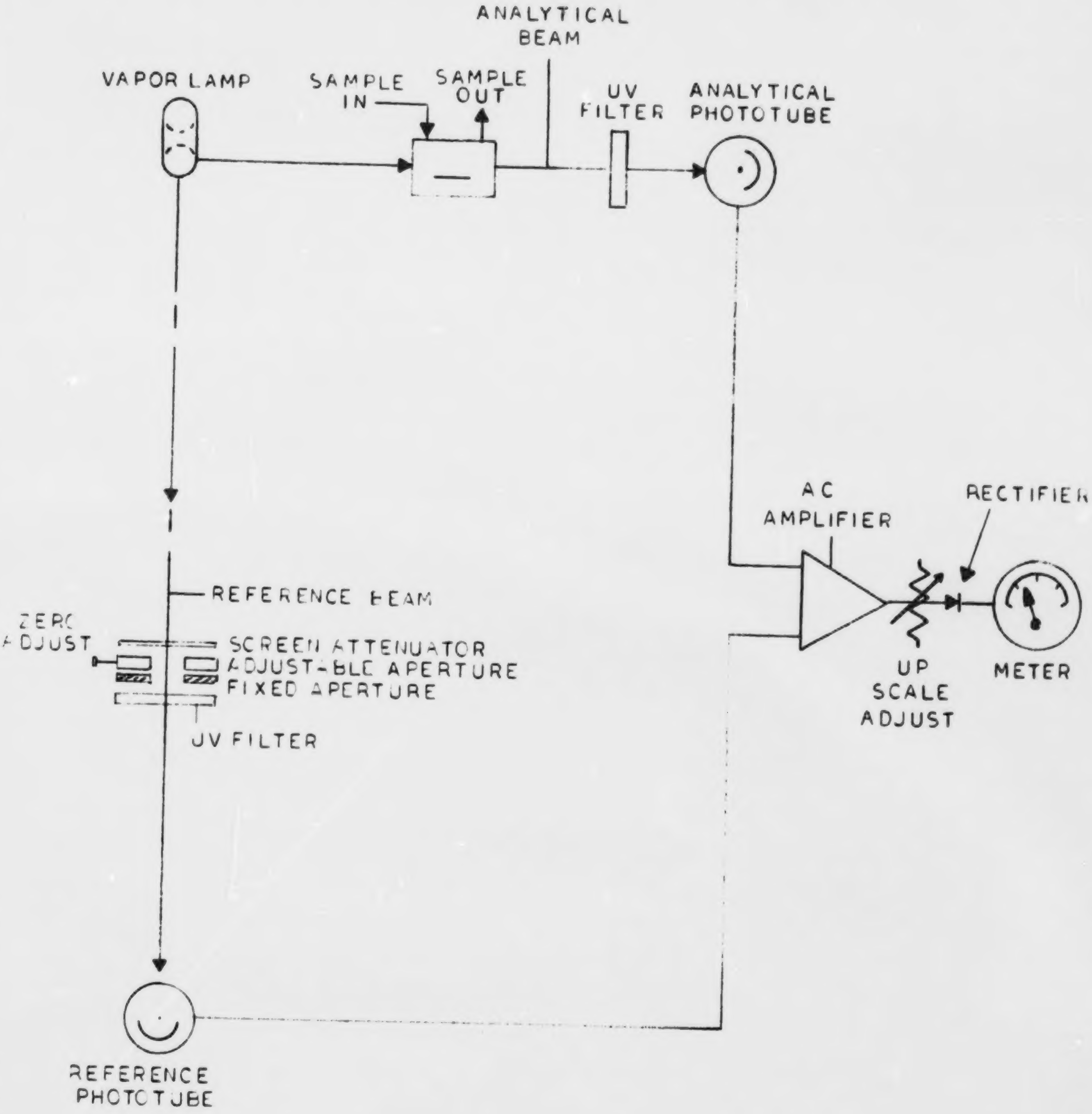
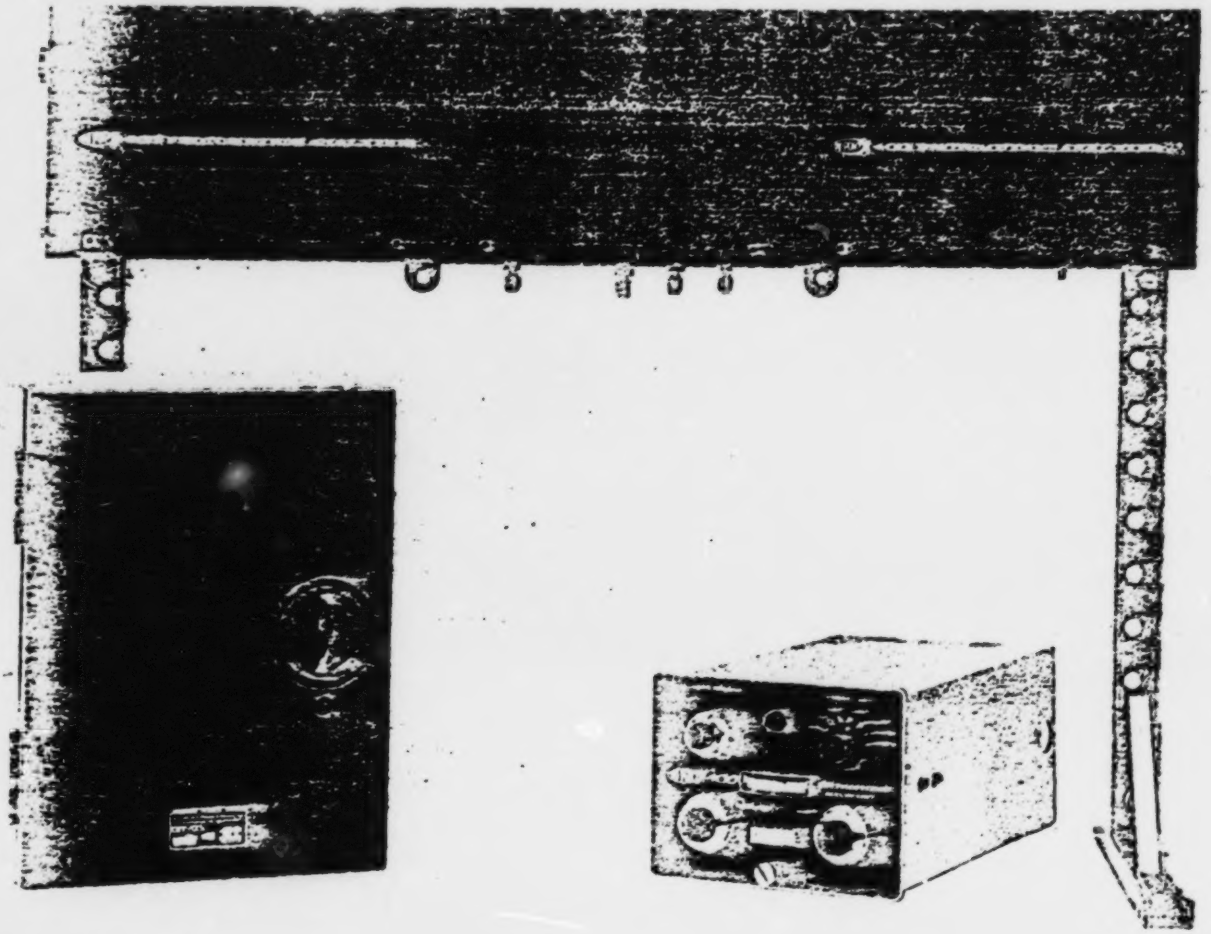
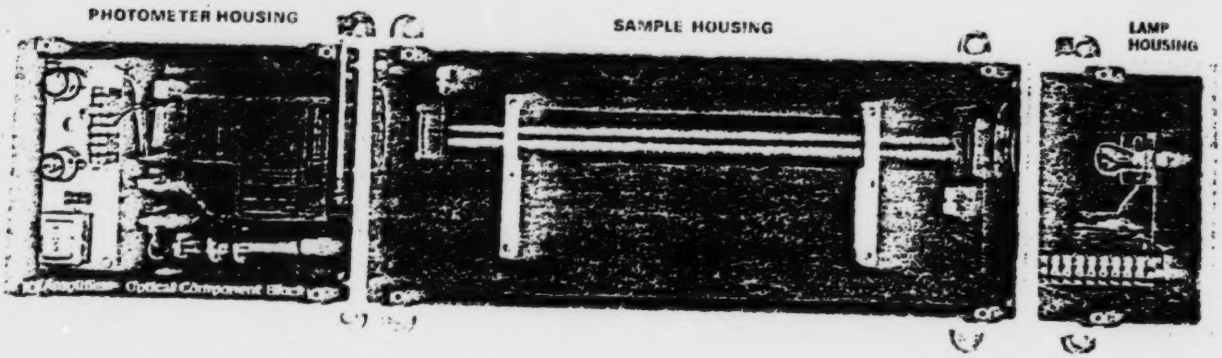

ANALYTICAL BEAM
VAPOR LAMP
SAMPLE IN
SAMPLE OUT
UV FILTER
ANALYTICAL PHOTOTUBE
AC AMPLIFIER
RECTIFIER
REFERENCE BEAM
ZERO ADJUST
SCREEN ATTENUATOR
ADJUSTABLE APERTURE
FIXED APERTURE
UV FILTER
UP SCALE ADJUST
METER
REFERENCE PHOTOTUBE

Figure 2-2. Operating Principle of Single Beam Instrument.



Typical Du Pont 400 Photometric Analyzer


PHOTOMETER HOUSING
SAMPLE HOUSING
LAMP HOUSING
Amplifier
Optical Component Block

Basic Analyzer

Figure 2-3. Dupont 400 Photometric Analyzer

Analyzer operation is based on the absorption of light by the sample material. Radiation from a Pen-Ray lamp passes through the sample and light at a wavelength of 253.7 nm is absorbed by the sample. Light transmitted through the sample is divided by a semi-transparent mirror into two beams and each beam then passes through its own optical filter bundle. Each filter bundle permits only a particular wavelength to reach its associated phototube. Optical filters in one beam permit only radiation at the measuring wavelength to pass through, whereas the optical filters in the second beam permits only light at the reference wavelength to pass through. Measuring and reference wavelengths were chosen so that sample constituents not to be measured would absorb light to the same degree. Thus, effects of variations in concentration of these interfering materials in the sample are minimized or eliminated. The operating principle is shown in Figure 2-4. The analyzer was provided with a twenty-inch Teflon cell and two quartz windows contained in a cell housing maintained at a temperature of 140°F. The instrument was adjusted for the measurement of mercury levels in the range of 0-1.0 milligrams per cubic meter.

During the field tests at the zinc smelter, the original cell was replaced with a two-inch Teflon cell.

4. Geomet Air Mercury Monitor

The Geomet Air Mercury Monitor (Figure 2-5) is a highly sensitive instrument designed to measure elemental and total mercury in air. The system can only determine elemental mercury in the vapor state, as do the other photometric analyzers, however; conversion to a particulate and gas analyzer for total mercury requires combination with a pyrolyzer.

The Geomet Air Mercury Monitor draws air into the grid section at a nominal flow rate of 175 liters per minute. Selected sampling rates are available by the use of limiting orifices. Mercury vapor is extracted from the air by two silver wire grids wound around a grid tube. At the

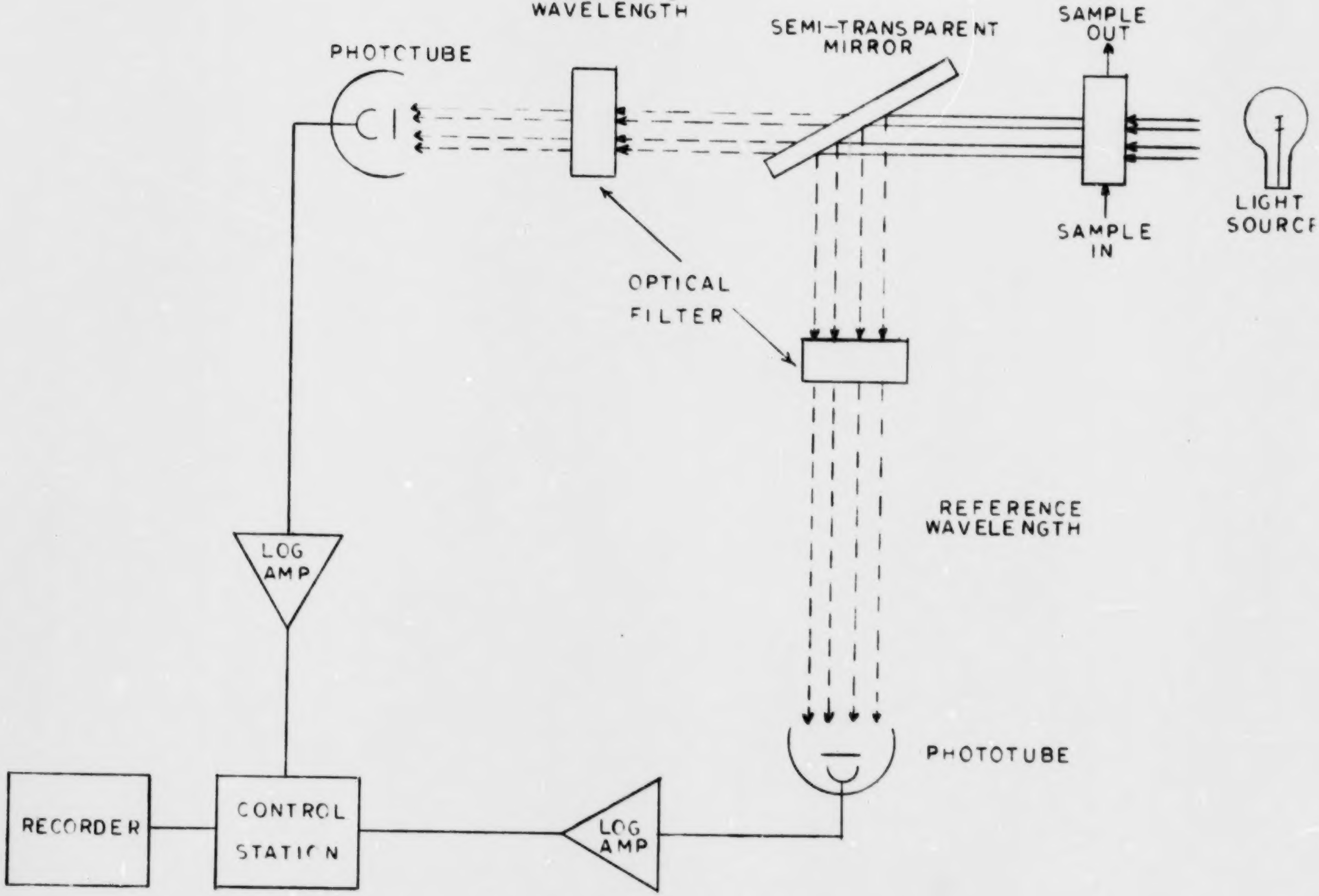

PHOTOTUBE
MEASURING WAVELENGTH
SEMI-TRANSPARENT MIRROR
SAMPLE OUT
LIGHT SOURCE
SAMPLE IN
OPTICAL FILTER
REFERENCE WAVELENGTH
LOG AMP
PHOTOTUBE
RECORDER
CONTROL STATION
LOG AMP

Figure 2-4. **Operating Principle of Dual-Wavelength Instrument.**

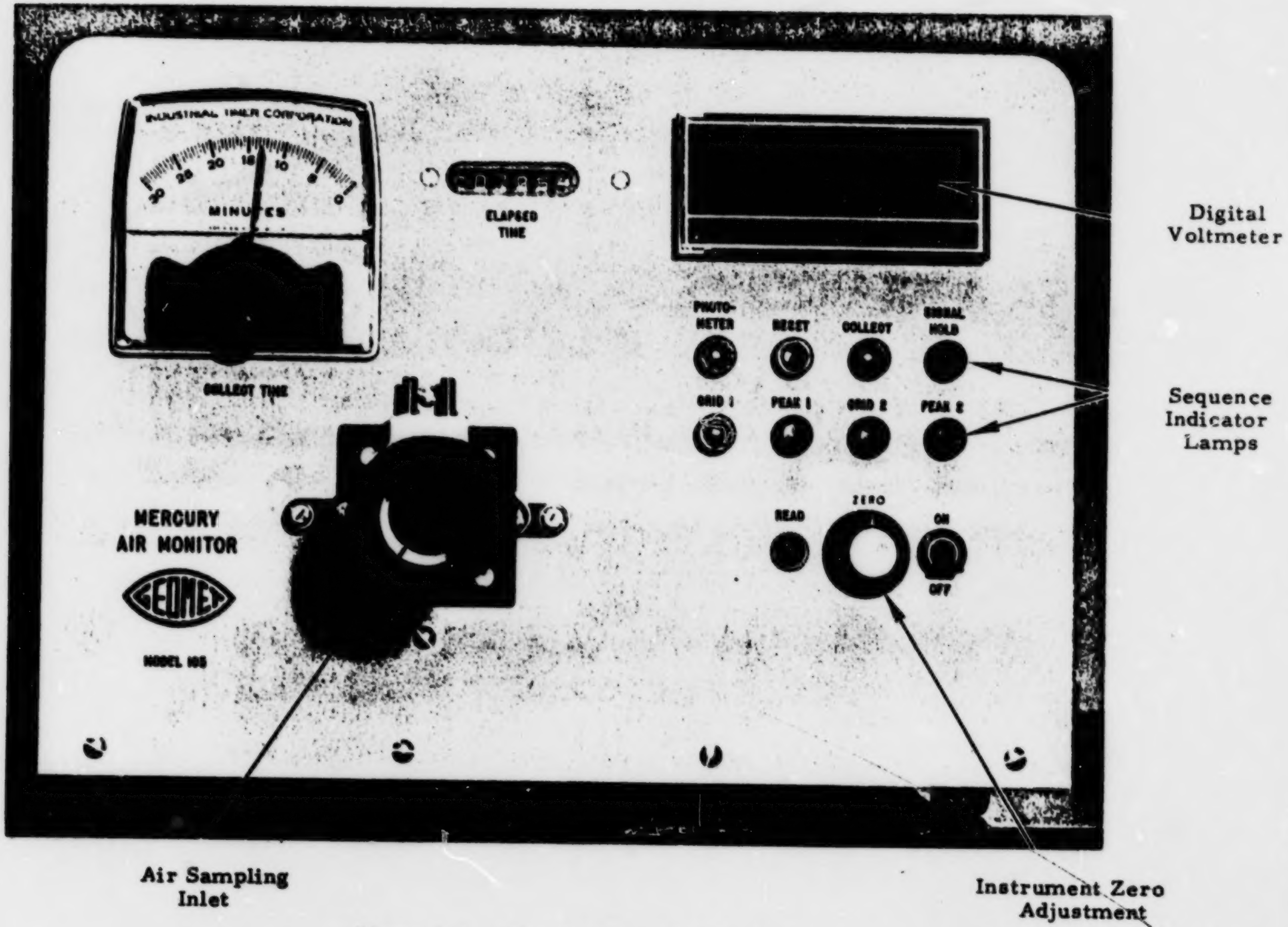

INDUSTRIAL TIMER CORPORATION
30 25 20 15 10 5 0
MINUTES
COLLECT TIME
ELAPSED TIME
MERCURY AIR MONITOR
GEOMET
MODEL 105
PHOTO-METER
RESET
COLLECT
SIGNAL HOLD
GRID 1
PEAK 1
GRID 2
PEAK 2
READ
ZERO
ON
OFF
Digital Voltmeter
Sequence Indicator Lamps
Air Sampling Inlet
Instrument Zero Adjustment

Figure 2-5. Geomet Mercury Air Monitor

end of the sampling period, these grids are consecutively heated to desorb collected mercury. The stored signal from grid one is equivalent to any collected interferences and is cancelled out upon final readout. During this process, the air flow valve is closed to divert air, at approximately 2.0 liters per minute, from the grid chamber through an ultraviolet photometer. The peak signal difference obtained when the two grids are heated is displayed in arbitrary units on a digital voltmeter.

For use in other than ambient levels of mercury, the air diluter (Figure 2-6) must be utilized. The diluter consists of a small manifold connected to a clean air inlet and a rotameter through which the sample stream (100-500 cc per minute) with a relatively large amount of clean air (16-20 liters per minute) pass. The clean air is created by passage through a bed of silver on alumina pellets (approximately 12% silver on 1/8" pellets). By closing the flow control valve (to avoid sampling the air except through the absorbent), the instrument should indicate zero. The air diluter was required throughout the program due to the sensitivity of the unit.

5. Olin Mercury Monitor, Gas

The Olin Mercury Monitor, Gas (Figure 2-7) detects elemental mercury vapor by ultraviolet light absorption with a Dupont 400 photometric analyzer (refer to section 3). The measurement is based on the utilization of stannous chloride as a reducing agent as this instrument was primarily designed for application in a chlor-alkali plant. The stannous chloride serves to remove excess halogen, such as chlorine, from the air sample, thereby preventing its recombination with mercury. Stannous chloride reacts with chlorine to form stannic chloride. A pyrolyzer was also incorporated in the Olin Monitor prior to the reducing agent for those applications that involve organic mercury compounds. Up to ten gas samples can be continuously drawn to the instrument by vacuum and chosen by a stream selector for analysis (Figure 2-8).

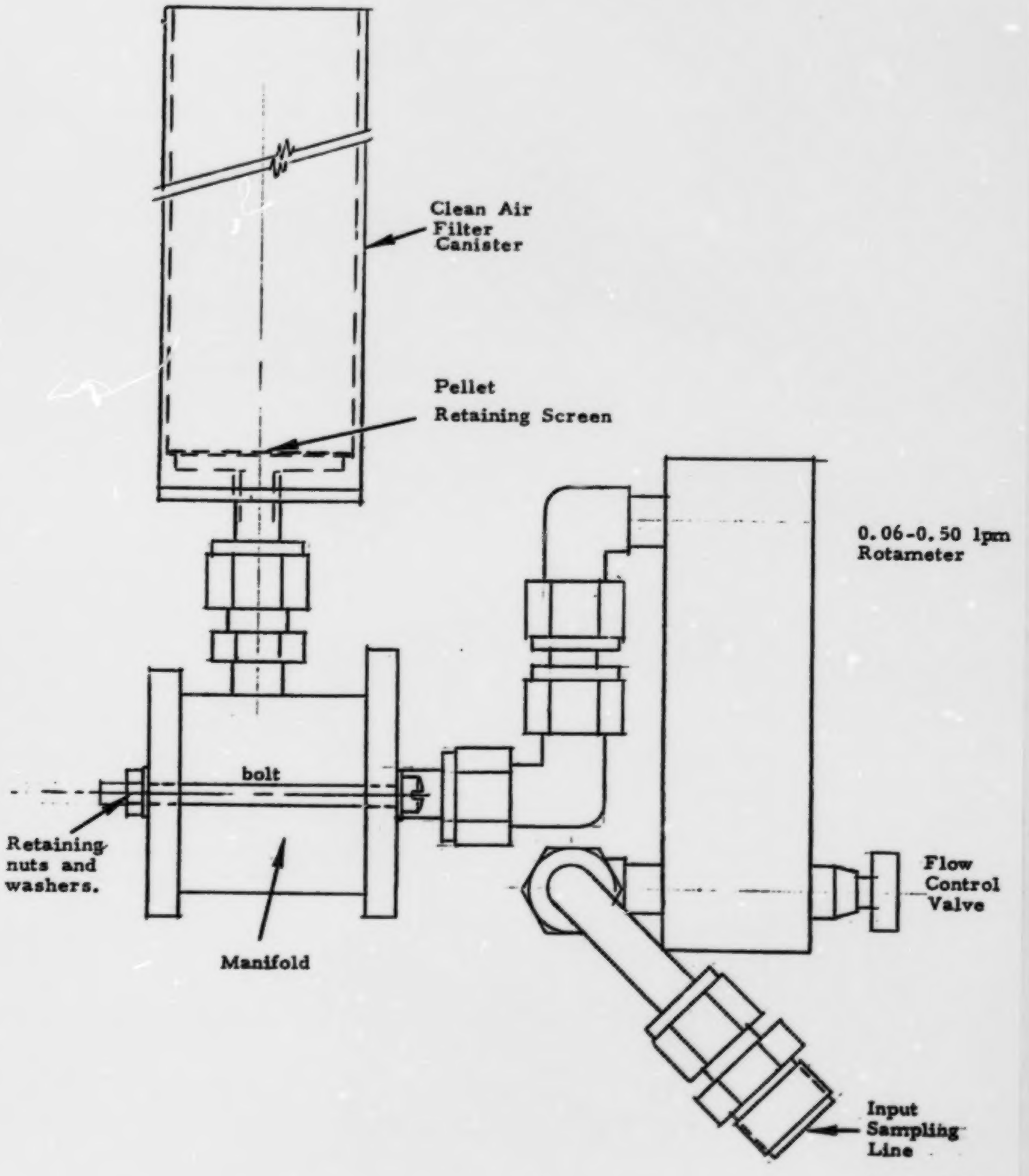

Clean Air
Filter
Canister
Pellet
Retaining Screen
0.06-0.50 lpm
Rotameter
bolt
Retaining
nuts and
washers.
Manifold
Flow
Control
Valve
Input
Sampling
Line
(from M109
tubing or
ambient air)

Figure 2-6. Geomet Air Dilution Kit

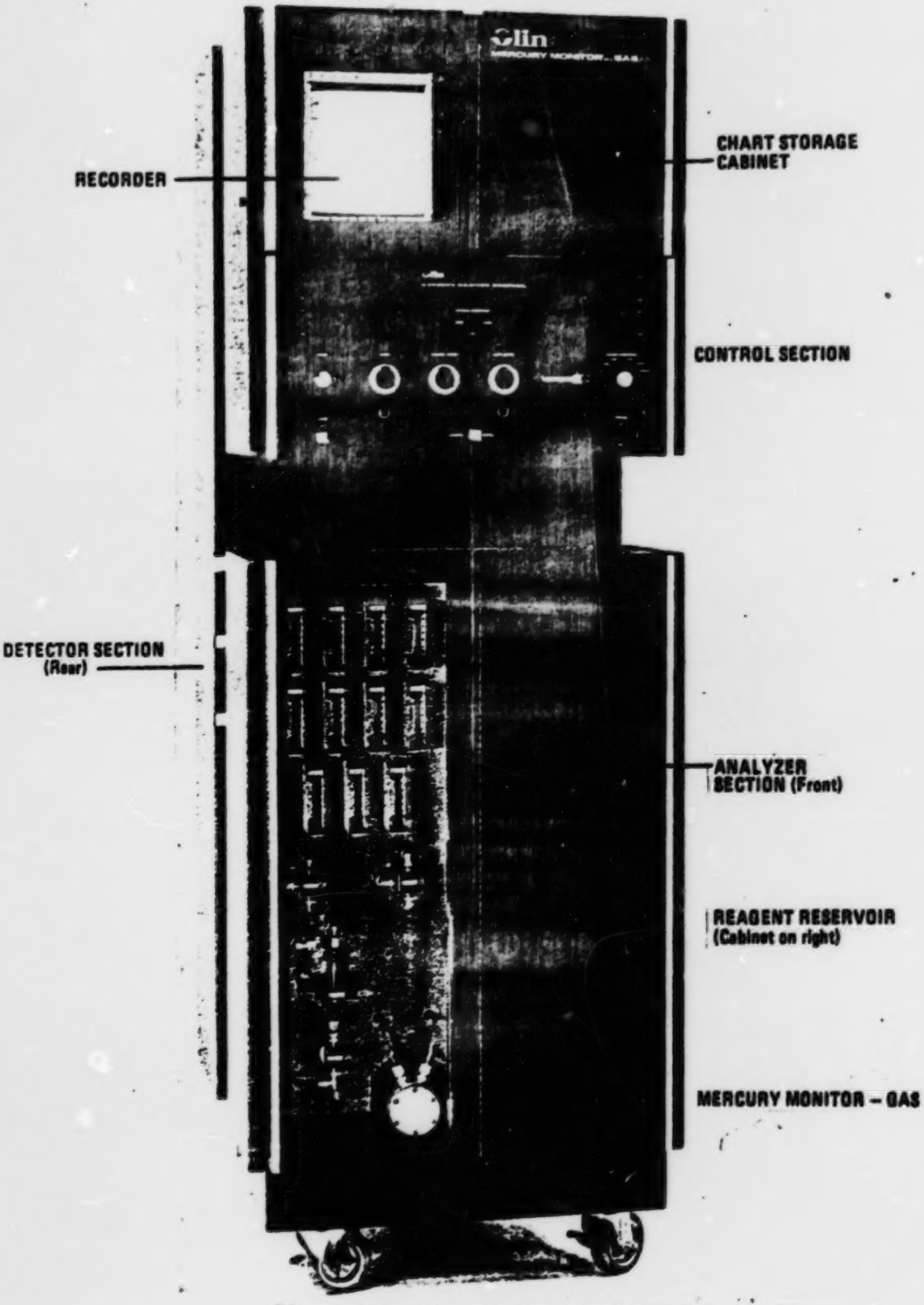

Olin
MERCURY MONITOR – GAS
RECORDER
CHART STORAGE CABINET
CONTROL SECTION
DETECTOR SECTION (Rear)
ANALYZER SECTION (Front)
REAGENT RESERVOIR (Cabinet on right)
MERCURY MONITOR – GAS

Figure 2-7. Olin Mercury Monitor, Gas

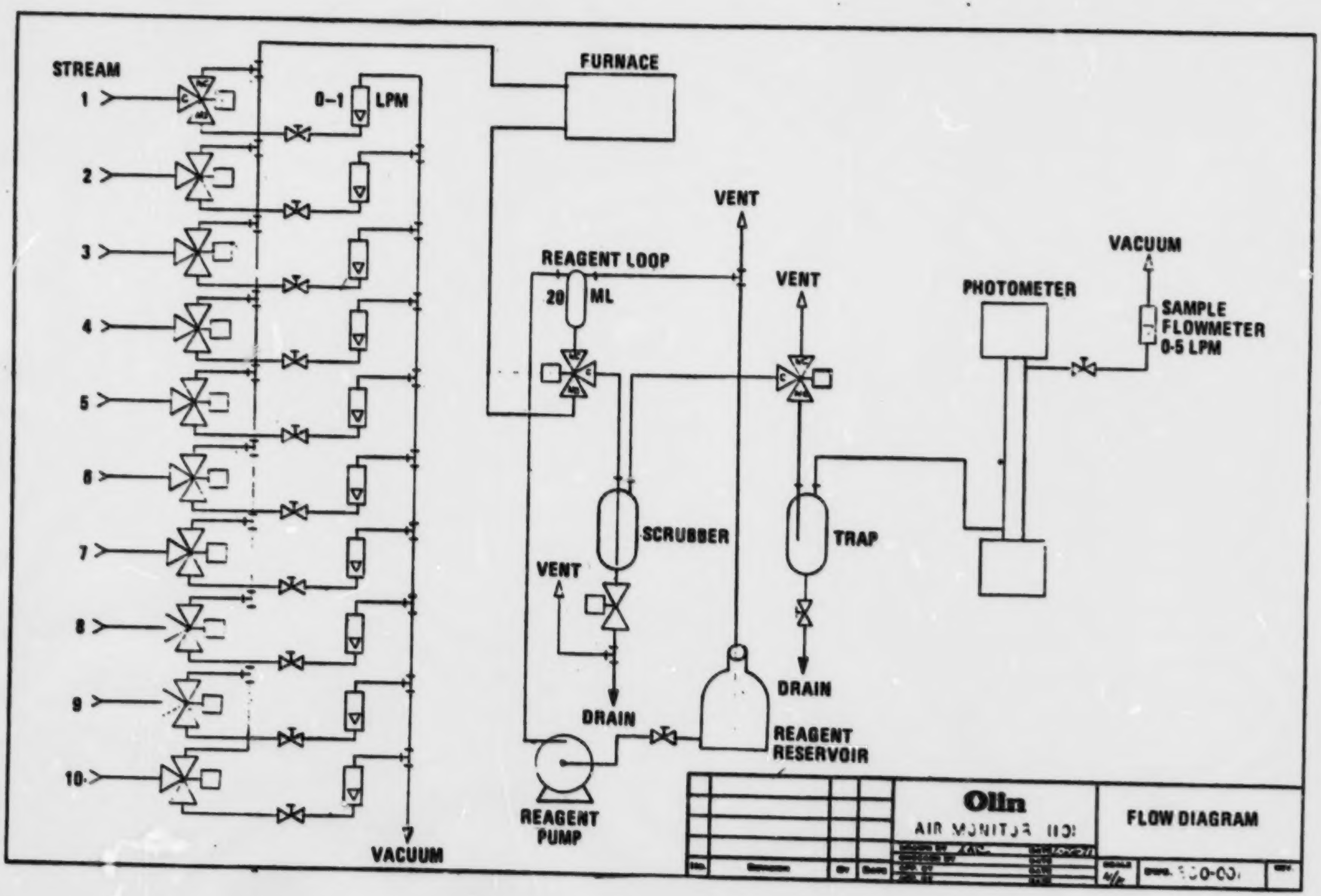

STREAM
1
2
3
4
5
6
7
8
9
10
0-1 LPM
VACUUM
FURNACE
REAGENT LOOP
20 ML
VENT
VENT
VENT
SCRUBBER
TRAP
DRAIN
DRAIN
REAGENT PUMP
REAGENT RESERVOIR
PHOTOMETER
VACUUM
SAMPLE FLOWMETER 0-5 LPM
Olin
AIR MONITOR
FLOW DIAGRAM

Figure 2-8. Schematic, Olin Mercury Monitor, Gas.

The reagent section of this instrument consists of a reagent reservoir, a reagent circulating pump, a reagent loop and a reagent solenoid. The reagent pump is energized by a timer-programmer to fill the reagent loop with overflow to the reagent reservoir. Activation of the reagent solenoid by a timer micro-switch drains the fixed reagent volume into the scrubber. The scrubber-reactor of this monitor is a glass chamber in which the reagent comes in contact with the gas sample to convert ionizable mercury salts, particulates or vapors to metallic mercury.

The pyrolyzer is a portable, temperature controlled furnace placed in the sample system prior to the scrubber. It houses a fifteen-foot quartz coil, through which the sample flows, and in which any interfering gaseous material such as aromatics are broken down. It also assures total mercury analysis for those applications where organic mercury is involved.

The Olin monitor was tested in the laboratory phase of the program and was only available for testing at the chlor-alkali facility in the field portion of the program. The stannous chloride scrubbing system was bypassed during the laboratory studies performed on the Olin.

6. Sunshine Instantaneous Vapor Detector

The Sunshine Instantaneous Vapor Detector (Figure 2-9) is a small, portable, ultraviolet photometer. It is set for a wavelength of 253.7 nanometers and is used to determine the vapor concentration of mercury in air. However, the instrument used in this study was adapted for monitoring gas samples by inserting a 10 x 25 mm stainless steel cell with quartz windows to transport the sample through the analytical beam. Inlet and outlet Tygon tubing lines were replaced with Teflon tubing and the calibration system supplied was modified for application with the cell.

The instrument employs basically the same principle of operations as that of the Beckman (Refer to section 2).

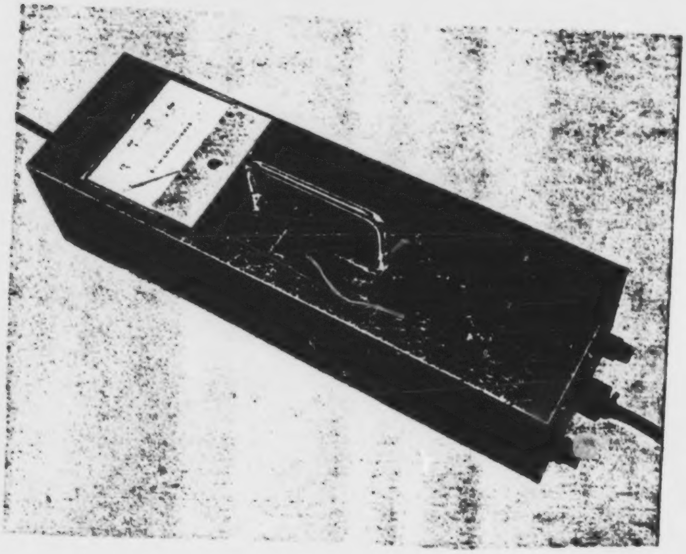


Figure 2-9. Sunshine Instantaneous Vapor Detector.

7. RAC Tape Stain Sampler

The RAC Tape Stain Sampler, AISI type (Figure 2-10) uses impregnated tapes to trap mercury vapor. The method is based on the reaction between active selenium sulfide and mercury vapor. The selenium sulfide is applied as a coating to paper and the coated paper is blackened on exposure to air containing mercury vapor, the degree of blackening being a function of time of exposure, concentration of mercury vapor, and other factors which can definitely be controlled.

The air or gas to be analyzed is blown into the apparatus by means of a small blower, the velocity of the sample stream being measured and controlled through a flowmeter. The air then passes over an electric heater to attain the proper temperature and into another tube, which ends in a nozzle. The selenium sulfide sensitized paper is exposed to the air containing the mercury vapor opposite the nozzle. The tape stain sampler suffers from interferences due to light, incomplete conversion of mercury compounds, and particulate matter.

The tape-stain sampler was modified by replacing the Tygon tubing with teflon tubing, adding a heating unit for the inlet line, and suppling charcoal traps on the outlet.

Initial attempts to prepare the selenium sulfide coated paper resulted in blotchy, uneven films having no uniformity. Some of the selenium sulfide powder was then suspended in ammonium sulfide solution (22%) and coated on strips of the paper drawn through a nip device. This coated paper when dried in a hood had an even consistency and the amount of coating applied could be varied by the speed with which it was drawn through the nip. The calibration technique of the tape-stain sampler involves calibration of the blackening of the paper against known mercury concentrations. This technique demands a relatively constant coating on the paper, a condition that could not be maintained at length.

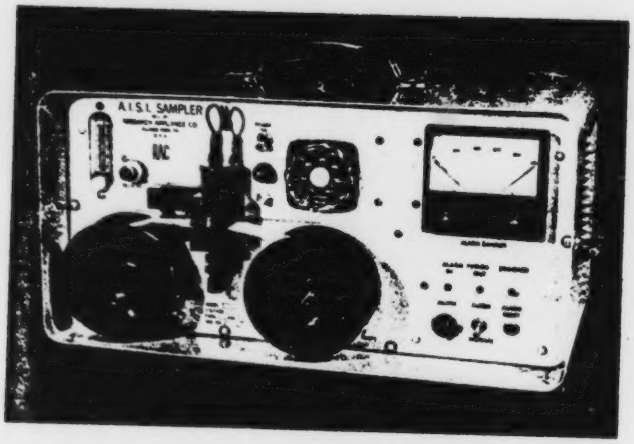

A.I.S.I. SAMPLER
RAC

Figure 2-10. RAC AISI Tape Stain Sampler

The basic principle of operation was applied in the laboratory. Nevertheless, the accuracy of this method was severely hampered by the variations in coating thickness. We also felt that the application of this instrument in the field would not adequately determine short-term variations in the concentration of mercury and, at best, the instrument would indicate relative variations.

Therefore, it was decided that the tape stain sampler would not be used in the remainder of the laboratory program or adapted for use in the field.

III. RESULTS OBTAINED IN THE WALDEN LABORATORY

A. DESCRIPTION OF MERCURY GENERATING SYSTEM

A schematic of the mercury generating system is shown in Figure 3-1. The intake air is drawn through a charcoal filter to remove any mercury or hydrocarbons from the air. The air is pumped through a Metal Bellows (M21) pump, a Moore low pressure flow controller, and then a calibrated orifice. This measured air stream bubbles through a flask containing mercury and water maintained at its boiling point. The vapors of water and mercury are refluxed and condensed and passed through an ice-cooled spiral-tube condenser that maintains the exit temperature at very nearly 0°C. The exit temperature is read from a thermometer placed in the gas stream. The purpose of the spiral condenser is to reduce the temperature sufficiently to ensure that the mercury vapor is saturated at that temperature. In that way, knowing the vapor pressure of mercury as a function of temperature (Table 3-1), the concentration of mercury can be calculated.

A dilution air stream is employed as a means for varying the mercury concentration in the working range of the monitoring instruments. Intake air is pumped through a charcoal filter and then a calibrated orifice. The measured dilution air is added to the mercury flow downstream of the spiral condenser and then passes through the mercury monitor. Finally, an evacuation pump serves to control the pressure at the inlet to the monitor and also vent the mercury vapor. An inclined manometer is connected to the inlet line to the monitor to determine the pressure. All lines and fittings contacting the mercury stream were either Teflon or glass.

The accuracy of the laboratory mercury-generating system was checked by comparison with samples of mercury collected in iodine monochloride. A Heath Model 700 atomic absorption analyzer operating in the flameless mode was used for the analysis of the mercury samples. The procedure for collection and analysis of mercury was a modified version of the EPA Regulations, Federal Register, April 6, 1973. The results of the

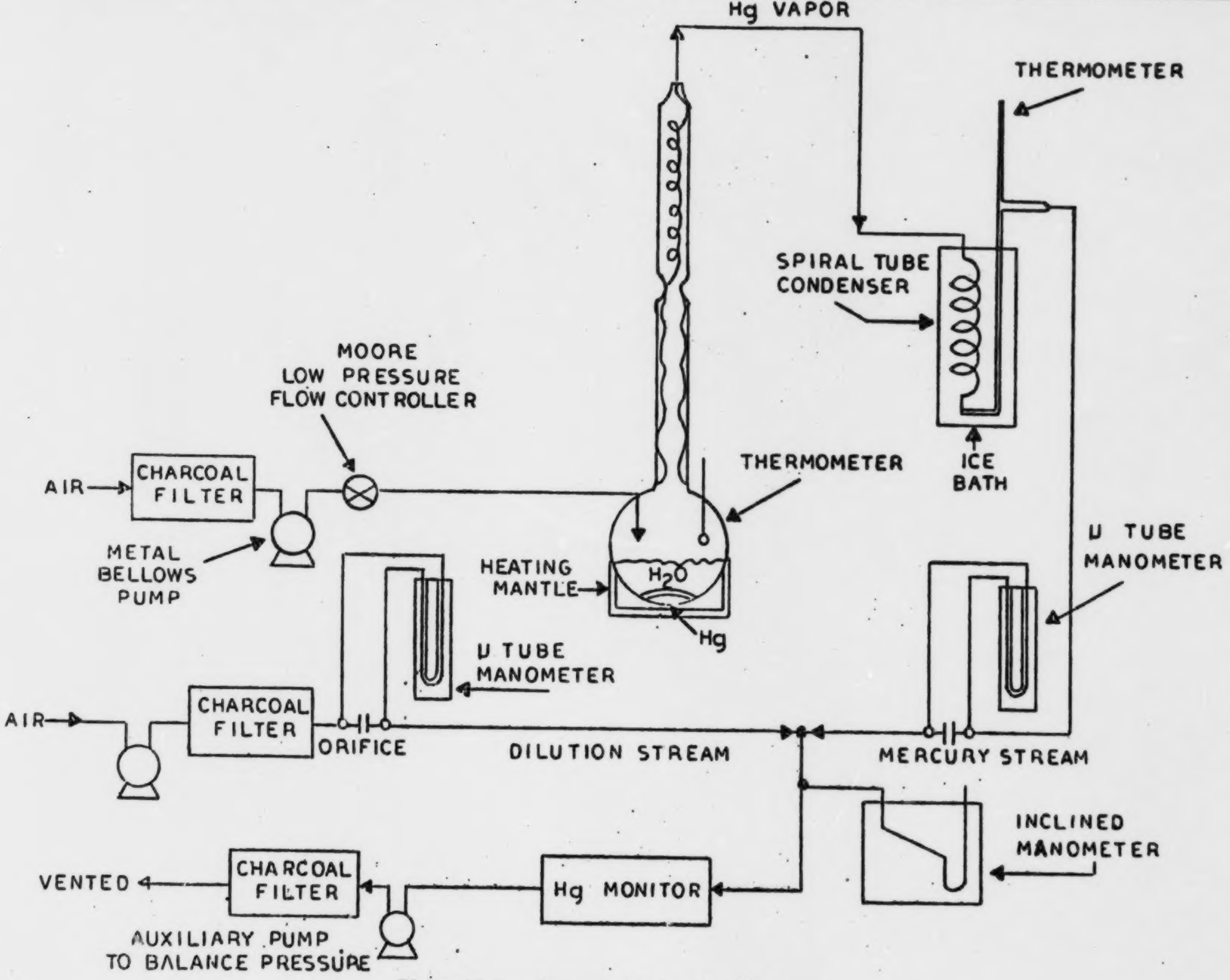

Hg VAPOR
THERMOMETER
SPIRAL TUBE CONDENSER
MOORE LOW PRESSURE FLOW CONTROLLER
AIR
CHARCOAL FILTER
METAL BELLOWS PUMP
THERMOMETER
ICE BATH
HEATING MANTLE
H_2O
Hg
U TUBE MANOMETER
U TUBE MANOMETER
AIR
CHARCOAL FILTER
ORIFICE
DILUTION STREAM
MERCURY STREAM
INCLINED MANOMETER
VENTED
CHARCOAL FILTER
Hg MONITOR
AUXILIARY PUMP TO BALANCE PRESSURE

Figure 3-1. Mercury Generating System.

TABLE 3-1

MERCURY CONCENTRATION (VAPOR PRESSURE) AS A FUNCTION OF TEMPERATURE

Temperature °C	Temperature °F	mm Hg(1)	ppm Hg(2)	mg Hg/m^3 (3)
0	32.0	0.000185	0.24	2.17
2	35.6	0.000228	0.30	2.66
4	39.2	0.000276	0.36	3.20
6	42.8	0.000335	0.44	3.85
8	46.4	0.000406	0.53	4.64
10	50.0	0.000490	0.64	5.56
12	53.6	0.000588	0.77	6.63
14	57.2	0.000706	0.93	7.90
16	60.8	0.000846	1.11	9.41
18	64.4	0.001009	1.33	11.14
20	68.0	0.001201	1.58	13.17
22	71.6	0.001426	1.88	15.54
24	75.2	0.001691	2.22	18.30
26	78.8	0.002000	2.63	21.50
28	82.4	0.002359	3.10	25.19
30	86.0	0.002777	3.65	29.46
32	89.6	0.003261	4.29	34.33
34	93.2	0.003823	5.03	40.03
36	96.8	0.004471	5.88	46.51
38	100.4	0.005219	6.87	53.95
40	104.0	0.006079	8.00	62.43
42	107.6	0.007067	9.30	72.12
44	111.2	0.008200	10.79	83.16
46	114.8	0.009497	12.50	95.71
48	118.4	0.01098	14.45	109.97
50	122.0	0.01267	16.67	126.11
52	125.6	0.01459	19.20	144.32
54	129.2	0.01677	22.07	164.88
56	132.8	0.01925	25.33	188.11
58	136.4	0.02206	29.03	214.27

TABLE 3-1 (continued)

Temperature °C	Temperature °F	mm Hg(1)	ppm Hg(2)	mg Hg/m^3 (3)
60	140.0	0.02524	33.21	243.68
62	143.6	0.02883	37.93	276.68
64	147.2	0.03287	43.25	313.59
66	150.8	0.08740	49.21	354.70
68	154.4	0.04251	55.93	400.80
70	158.0	0.04825	63.49	452.27
72	161.6	0.05469	71.96	509.66
74	165.2	0.06189	81.43	573.44
76	168.8	0.06993	92.01	644.22
78	172.4	0.07889	103.80	722.63
80	176.0	0.08880	116.84	808.80
82	179.6	0.1000	131.58	905.68
84	183.2	0.1124	147.89	1012.29
86	186.8	0.1261	165.92	1129.35
88	190.4	0.1413	185.92	1258.47
90	194.0	0.1582	208.16	1401.23
92	197.6	0.1769	232.76	1558.28
94	201.2	0.1976	260.00	1731.15
96	204.8	0.2202	289.74	1918.69
98	208.4	0.2453	322.76	2125.88
100	212.0	0.2729	359.08	2352.40

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(1) From "Handbook of Chemistry" by Lange, N. A., 1952, pp. 1499-1500.

(2) $\text{ppm Hg} = \frac{\text{mm Hg}}{760\text{ mm}} \times 10^6$

(3) $\frac{\text{mg Hg}}{\text{m}^3} = \frac{\text{mm Hg}}{760\text{ mm}}\ \frac{200.59\text{ g Hg/mole}}{22.414\text{ l/mole}}\ \frac{273.2°}{273.2°+°\text{C}}\ \frac{10^3\text{ mg}}{\text{g}}\ \frac{10^3\text{ l}}{\text{m}^3}$

AA analysis compared to the calculated concentrations of the generating system are shown in Table 3-2. Two of the three preliminary analyses taken in February 1973 averaged within fifteen percent of the calculated value. Additional work was performed to improve the reliability of the AA analysis prior to the tests run in May 1973. The revised AA procedure gave close agreement with the calculated results as tests 4 through 8 were within ten percent of the calculated values.

TABLE 3-2

COMPARISON OF MERCURY GENERATING SYSTEM AND AA ANALYSIS

Run No.	Date	Mercury Generated by Calculation (μgm)	Mercury Collected by AA Analysis (μgm)
1	2/20	28.9	16.6
2	2/20	35.0	31.0
3	2/21	21.8	18.5
4	5/3	39.2	43.0
5	5/3	20.4	21.2
6	5/4	20.3	21.4
7	5/8	29.0	30.9
8	5/8	25.9	23.7

B. INTERFERENCES

1. Pyrolyzers for Removal of Hydrocarbons and Particulate Mercury Compounds

Three pyrolyzer units, the Geomet catalytic converter, a quartz tube pyrolyzer, and the Olin quartz tube pyrolyzer, were evaluated for the removal of hydrocarbons and particulate mercury compounds. The Geomet catalytic converter was employed in the field sampling system due to its ability to convert hydrocarbons at a lower temperature than the other pyrolyzers and its durable construction.

The quartz tube pyrolyzer consisted of a straight quartz tube 60 cm x 2.5 cm (with a volume of 423 cc) inside a tube furnace. The temperature of the furnace was controlled by a variable auto-transformer with an iron-constantan thermocouple wire inserted along the quartz tube wall. About 50 percent of the length of the quartz tube was in the furnace.

The Olin quartz tube pyrolyzer consisted of a fifteen foot coiled quartz tube within a Hotpack Corp. muffle furnace. This pyrolyzer was incorporated into the Olin monitor in front of the scrubber.

The Geomet catalytic converter normally contains alumina catalyst in a stainless steel reactor with stainless steel tubing. The air sampling rate of the Geomet ranges up to thirty liters per minute and operates at temperatures up to 800°C. The alumina pellets were removed from the furnace upon notification from Geomet, Inc. that this bed packing tended to adsorb mercury during high level tests.

2. Hydrocarbon Conversion

Laboratory tests were performed to evaluate the hydrocarbon conversion efficiency of the three pyrolyzer units. Since hydrocarbons, in particular aromatics, act as interferents for the ultraviolet analyzers, it is necessary to convert the organic species to non-absorbing species (CO_2) in our field sampling system. Samples of known quantities of hydrocarbons were made up by injecting measured amounts of hydrocarbons into mylar bags and diluting with charcoal-filtered air. The gas samples were then pumped through the converter being tested and the effluent stream captured in another mylar bag. The converted samples were introduced into a Beckman 400 hydrocarbon analyzer to determine the ppm of unconverted hydrocarbons.

Methane and ethylene were pumped through the quartz tube pyrolyzer at a flow rate of 6.4 liters per minute. Figures 3-2 and 3-3 show that this unit, at its maximum temperature of 1205°C was capable of only a 77 and 98 percent conversion of methane and ethylene, respectively.

The Geomet catalytic converter (containing the alumina catalyst) was initially tested and at a later time with the catalyst removed.

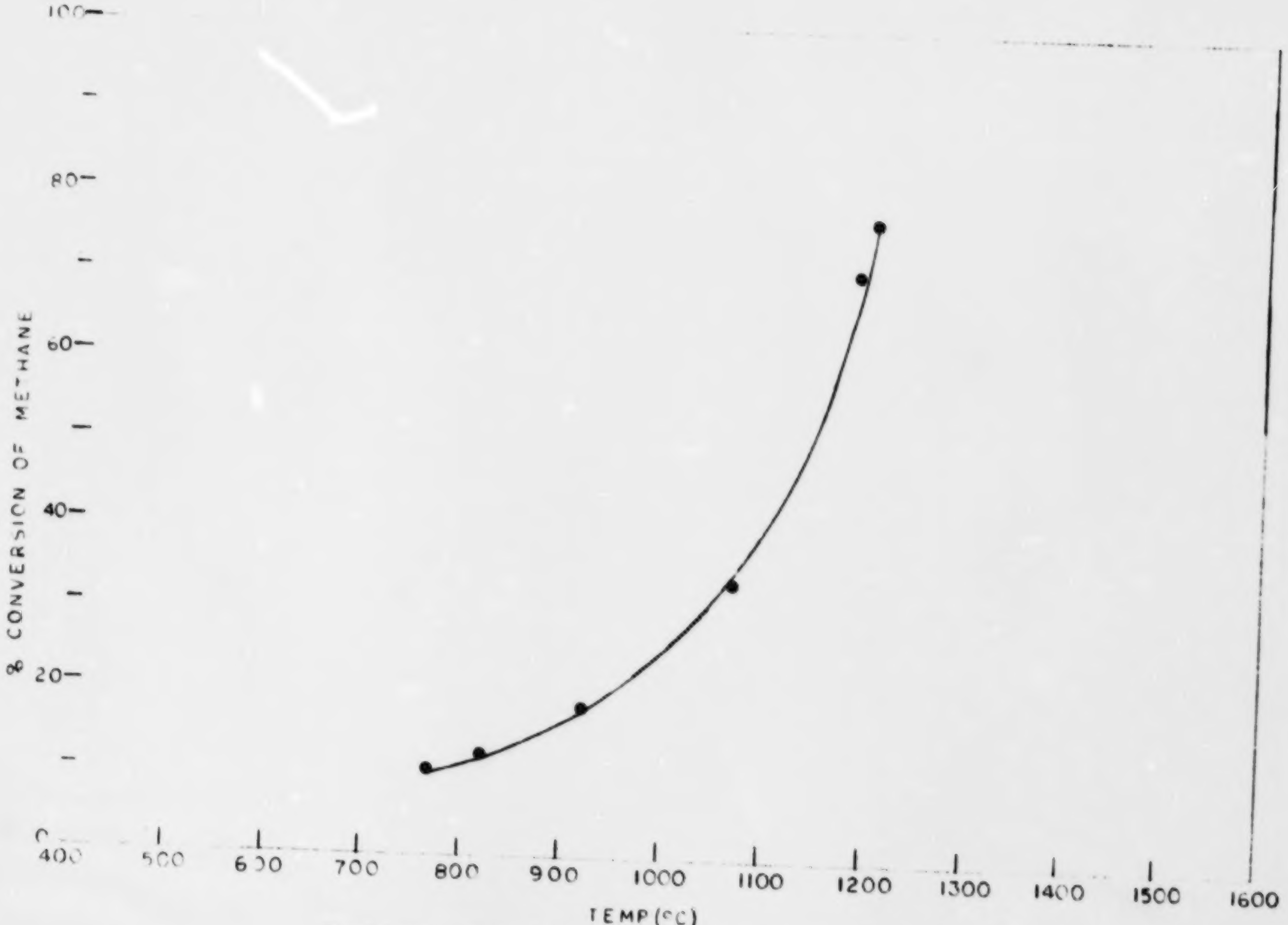


Figure 3-2. Conversion of Methane with a Quartz Tube Pyrolyzer

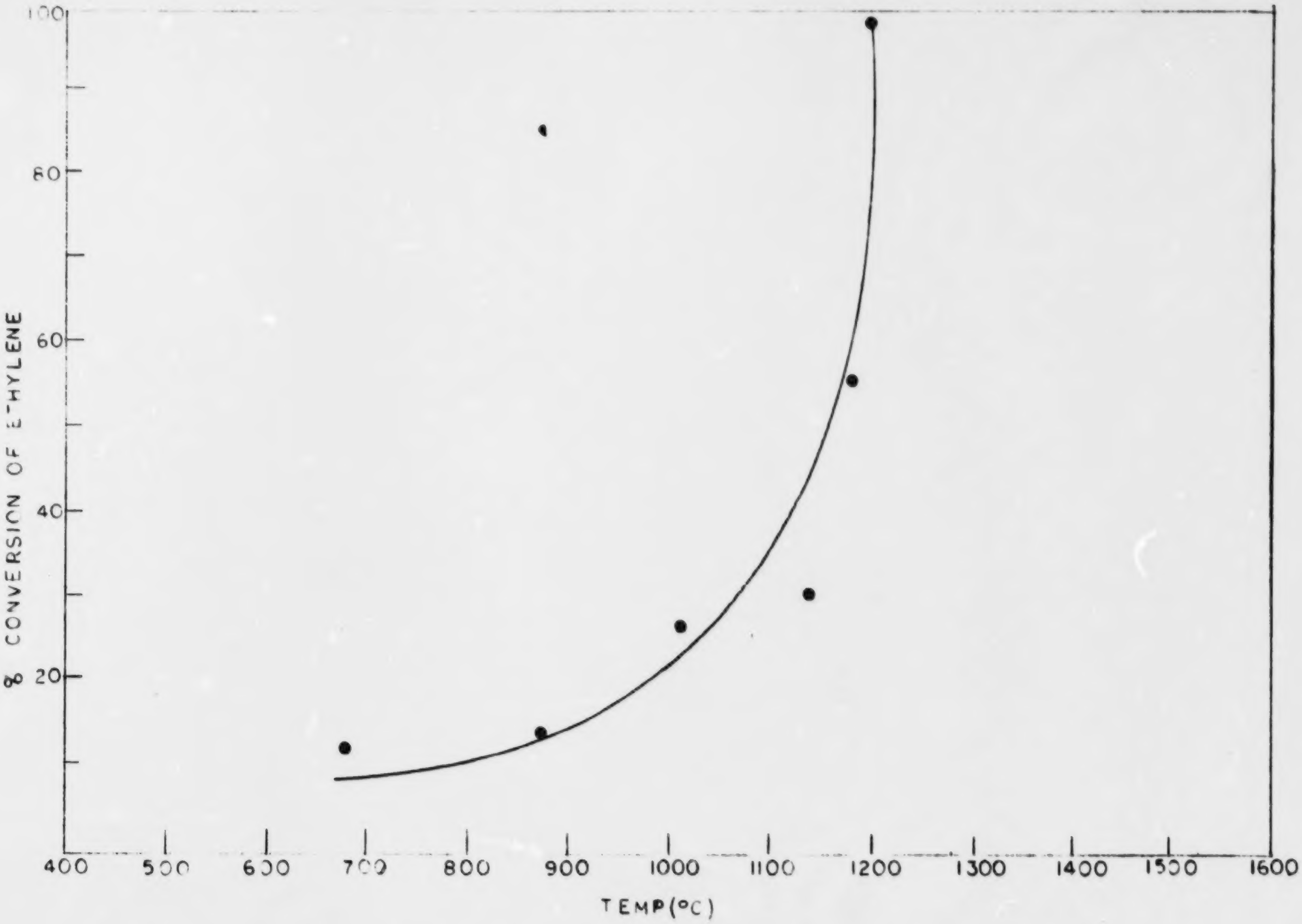


Figure 3-3. Conversion of Ethylene with a Quartz Tube Pyrolyzer

The tests with the catalyst were at a flow rate of 34 liters per minute while the tests without catalyst were performed at a flow rate of 28.3 liters per minute. It should be noted that the field system would require a pyrolyzer flow rate of only approximately one liter per minute. Figures 3-4 and 3-5 indicate that the Geomet converter with catalyst provides 100 percent conversion of methane and ethylene at temperatures of 690°C and 670°C, respectively. Figures 3-6 and 3-7 show that the Geomet unit without catalyst provides 100 percent conversion of ethylene and benzene at temperatures of 760°C and 860°C, respectively.

Methane was pumped through the Olin pyrolyzer at a flow rate of 4.5 liters per minute. Figure 3-8 indicates that methane was 100 percent converted at a temperature of 850°C.

It was concluded that the Geomet catalytic converter without the catalyst would convert all hydrocarbons at a flow rate of one liter per minute within its working temperature range. Therefore, the Geomet unit was employed as the pyrolyzer in the field sampling system.

3. Decomposition of Mercuric Chloride Aerosol

Since mercuric chloride aerosol might occur in chlor-alkali plant effluents, the thermal decomposition of mercuric chloride aerosol was investigated. A block diagram of the generating and decomposing system for mercuric chloride aerosol is shown in Figure 3-9.

The quartz tube pyrolyzer served to decompose the mercuric chloride to elemental mercury and chlorine. The Beckman monitor was employed to measure the mercury concentration as a function of pyrolyzer temperature. A flow rate of one liter per minute was maintained. The effect of pyrolyzer temperature on the decomposition of mercuric chloride aerosol is shown in Figure 3-10a and 3-10b. The data indicates that at least a temperature of 900°C is required to convert mercuric chloride to mercury in the quartz tube pyrolyzer.

Geomet, Inc. performed tests with mercury compounds concluding that the alumina catalyst in the catalytic converter is not absolutely

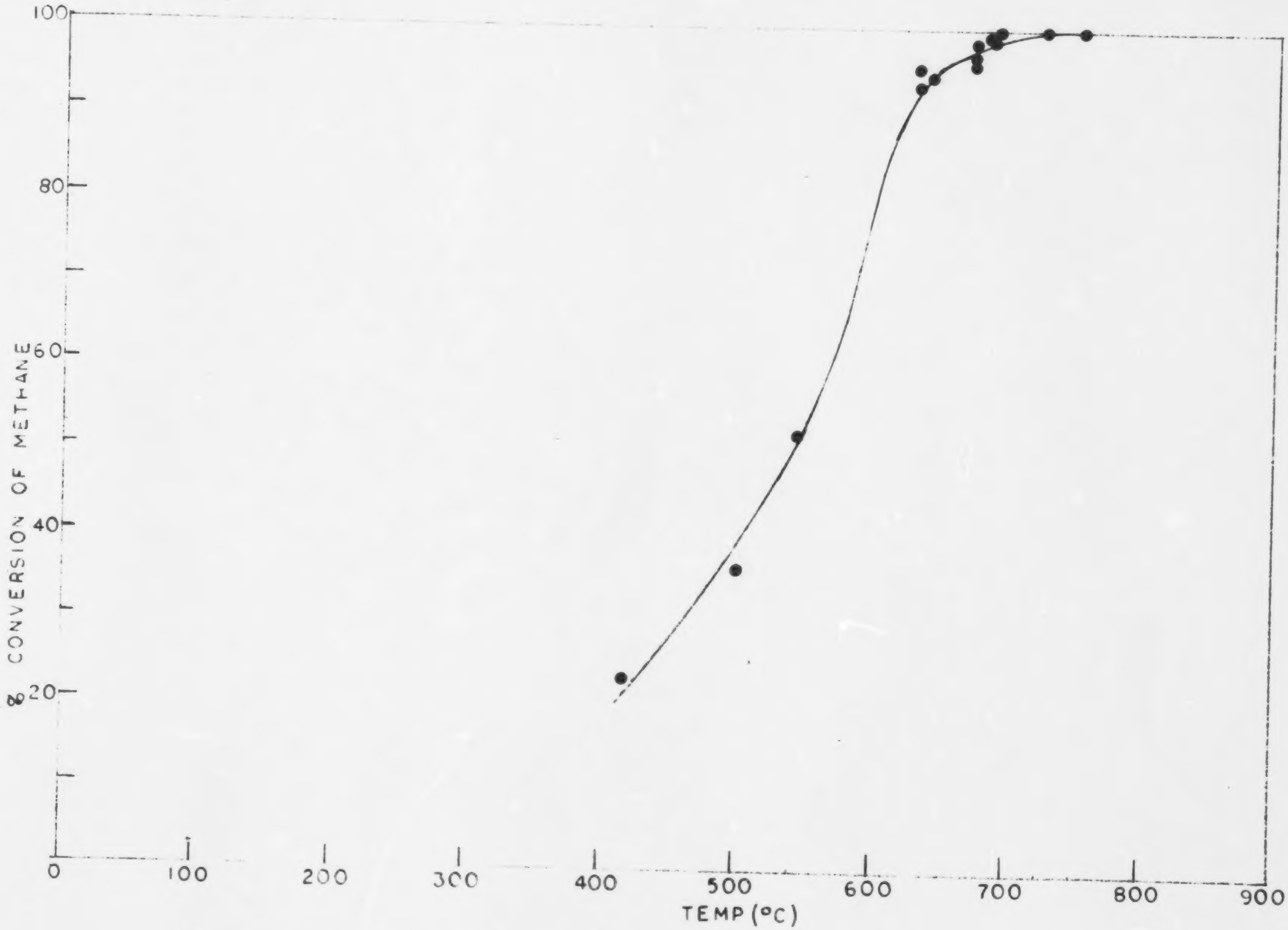


Figure 3-4. Conversion of Methane with the Geomet Catalytic Converter (with Catalyst)

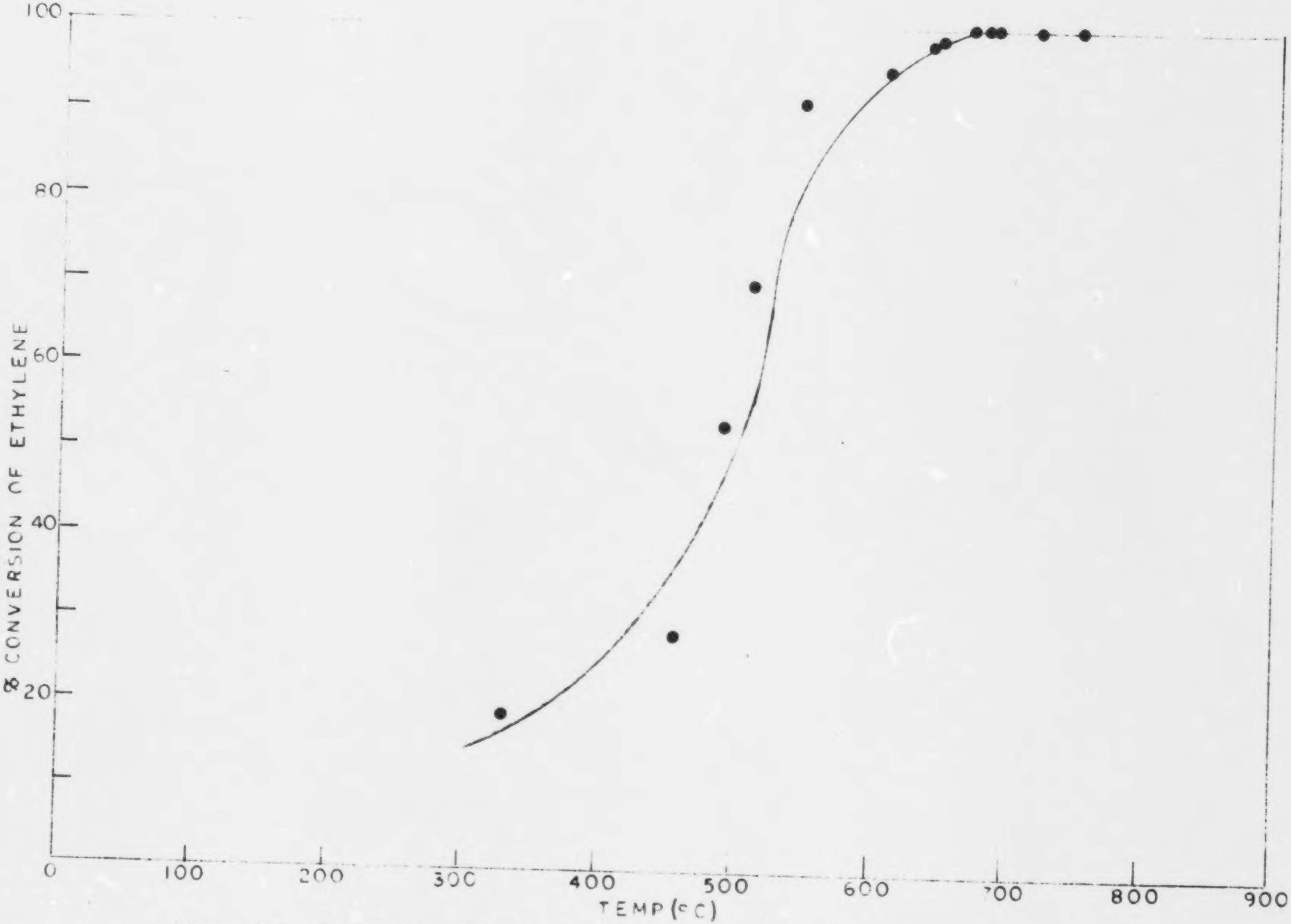


Figure 3-5. Conversion of Ethylene with the Geomet Catalytic Converter (with Catalyst).

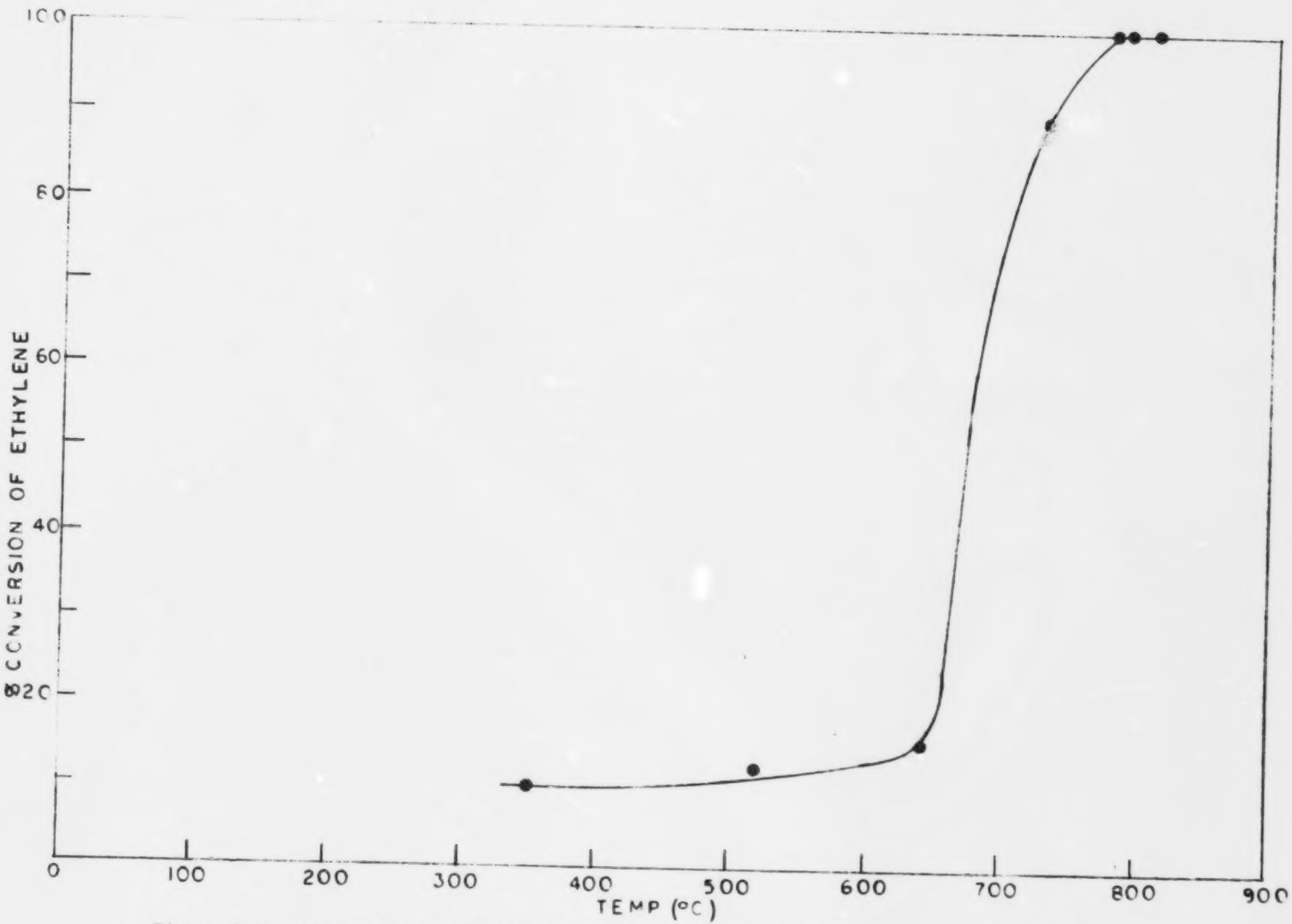


Figure 3-6. Conversion of Ethylene with the Geomet Catalytic Converter (without Catalyst).

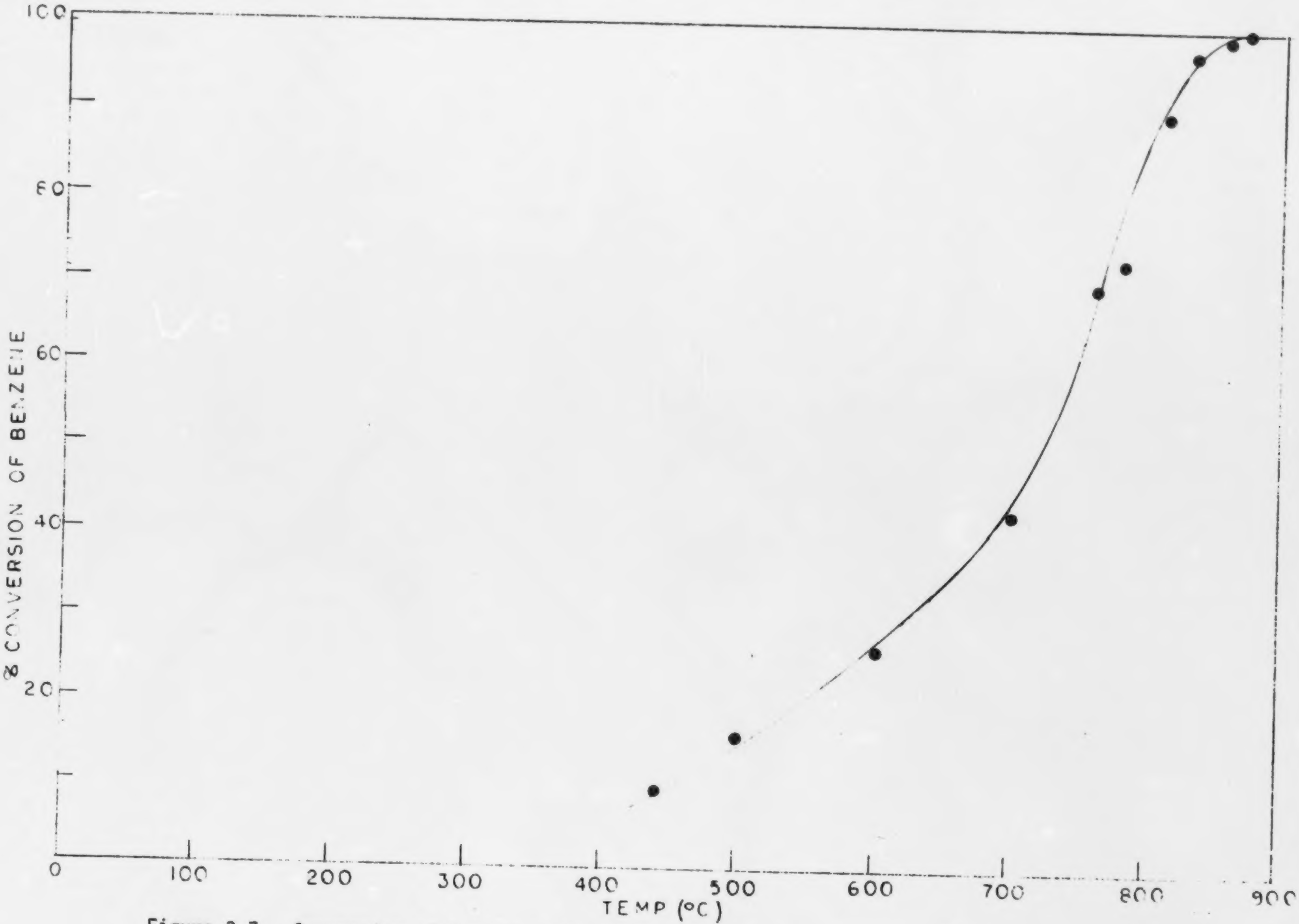


Figure 3-7. Conversion of Benzene with the Geomet Catalytic Converter (without Catalyst).

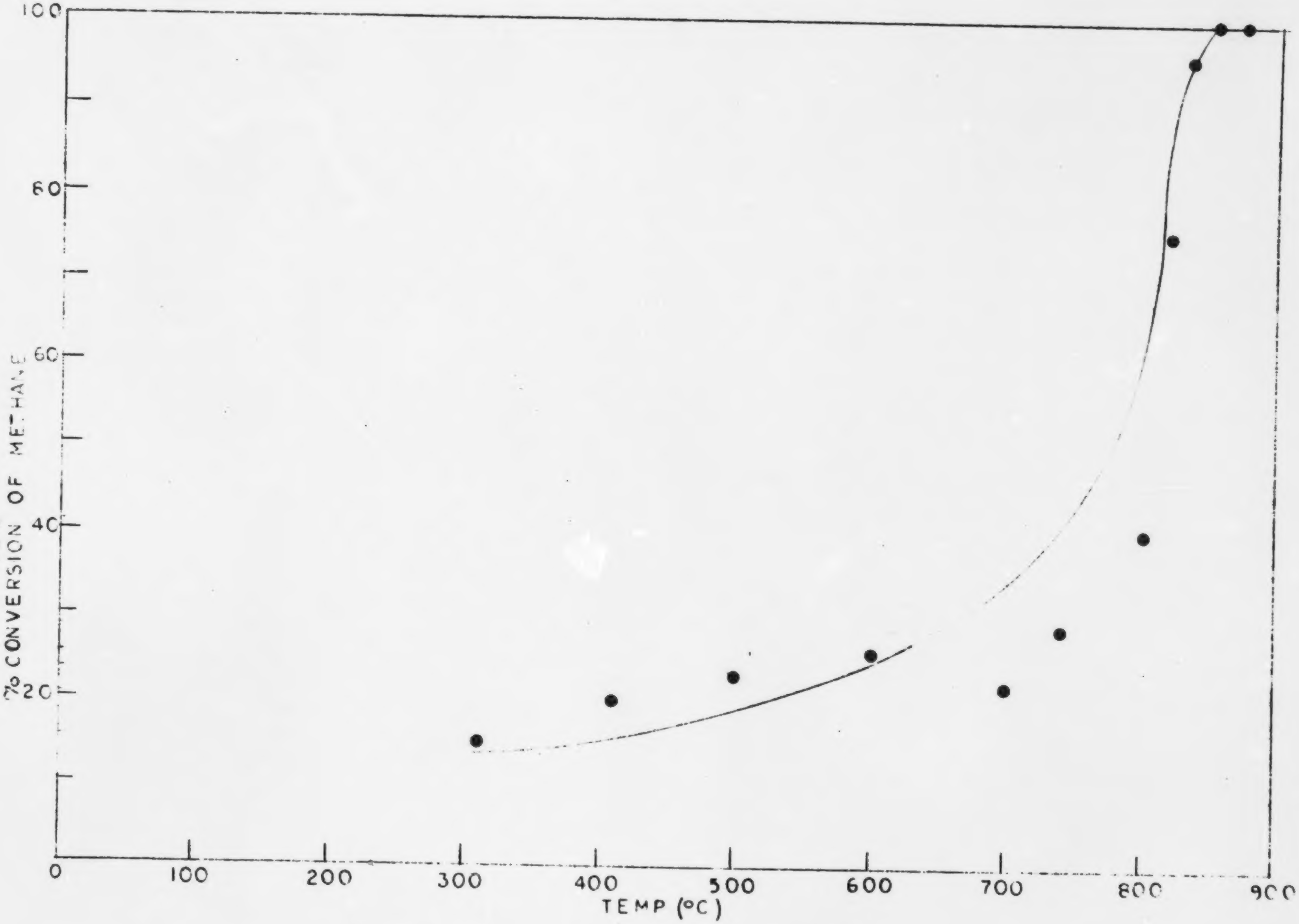
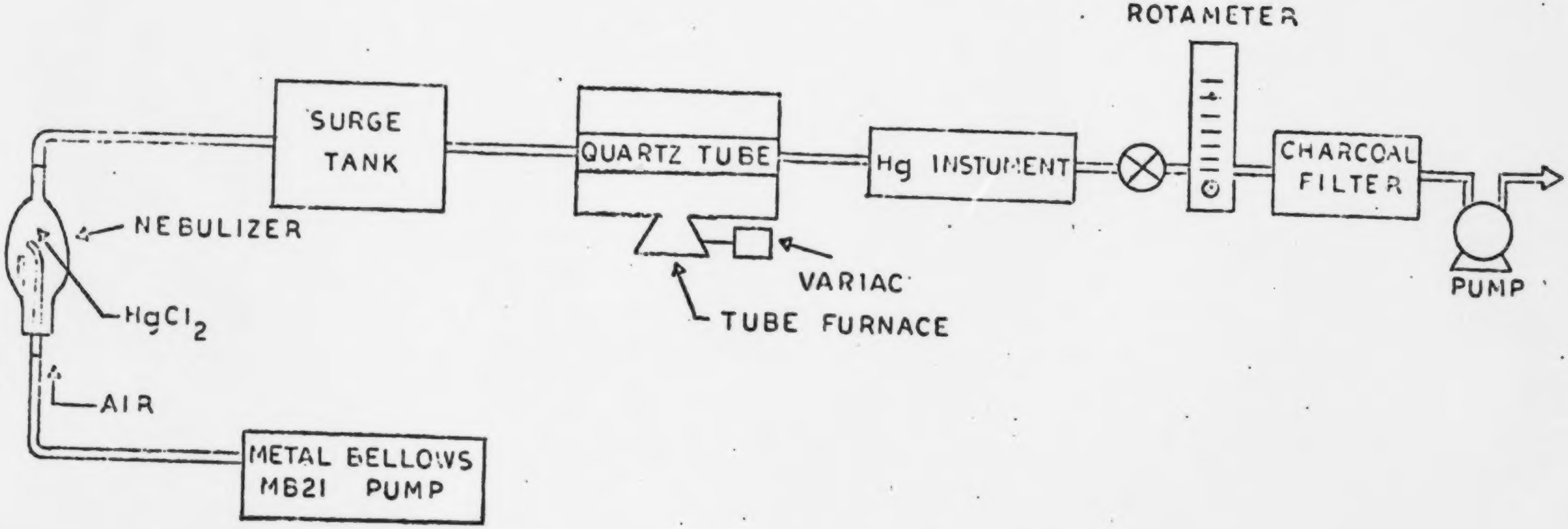


Figure 3-8. Conversion of Methane with the Olin Pyrolyzer.


ROTAMETER
SURGE TANK
QUARTZ TUBE
Hg INSTUMENT
CHARCOAL FILTER
NEBULIZER
VARIAC
PUMP
$HgCl_2$
TUBE FURNACE
AIR
METAL BELLOWS MB21 PUMP

NOTE: ALL LINES ARE TEFLON WITH GLASS CONNECTORS

Figure 3-9. Laboratory System for Generation and Decomposition of Mercuric Chloride Aerosol.

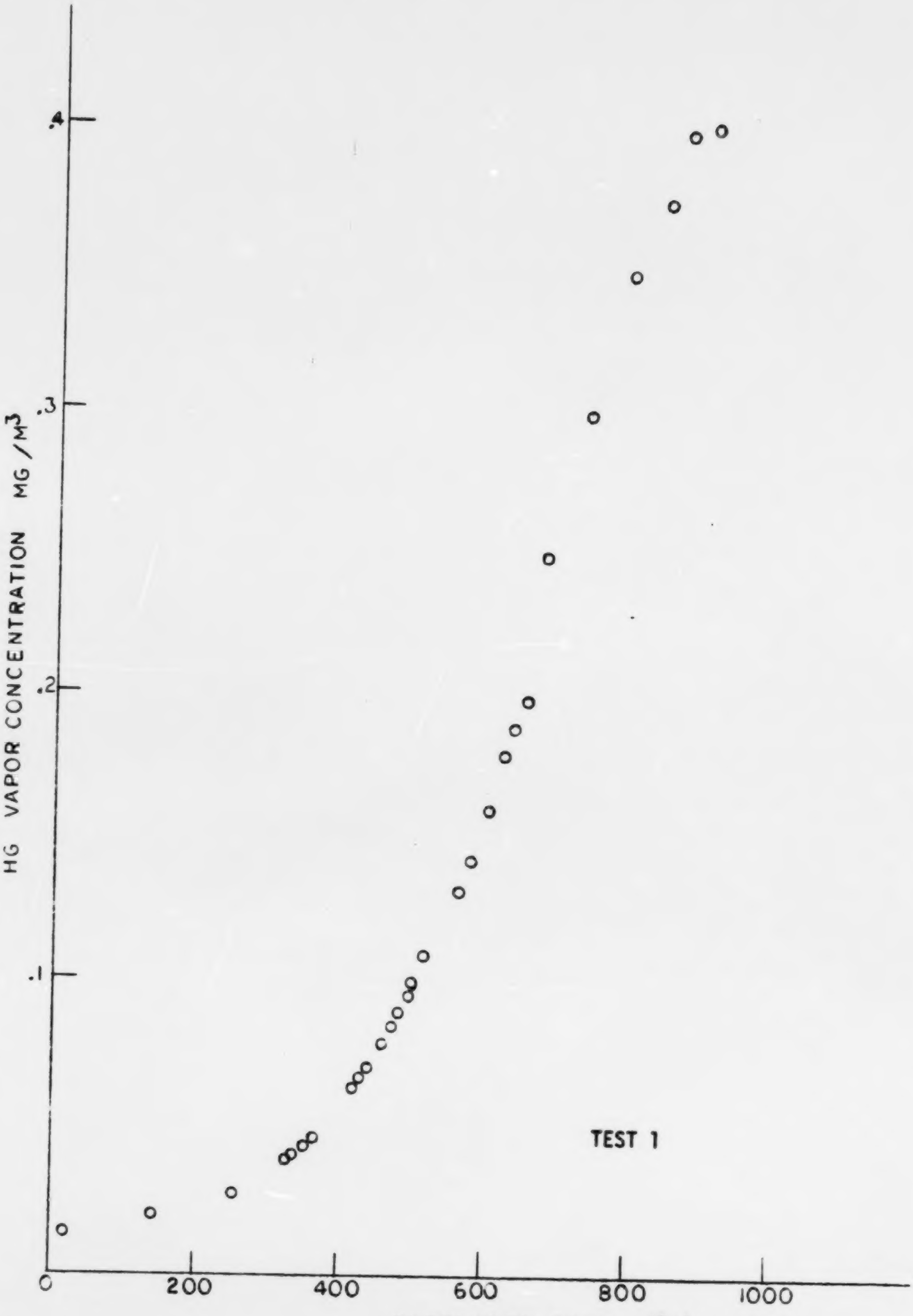


Figure 3-10a. Effect of Pyrolyzer Temperature in the Decomposition of Mercuric Chloride Aerosol.

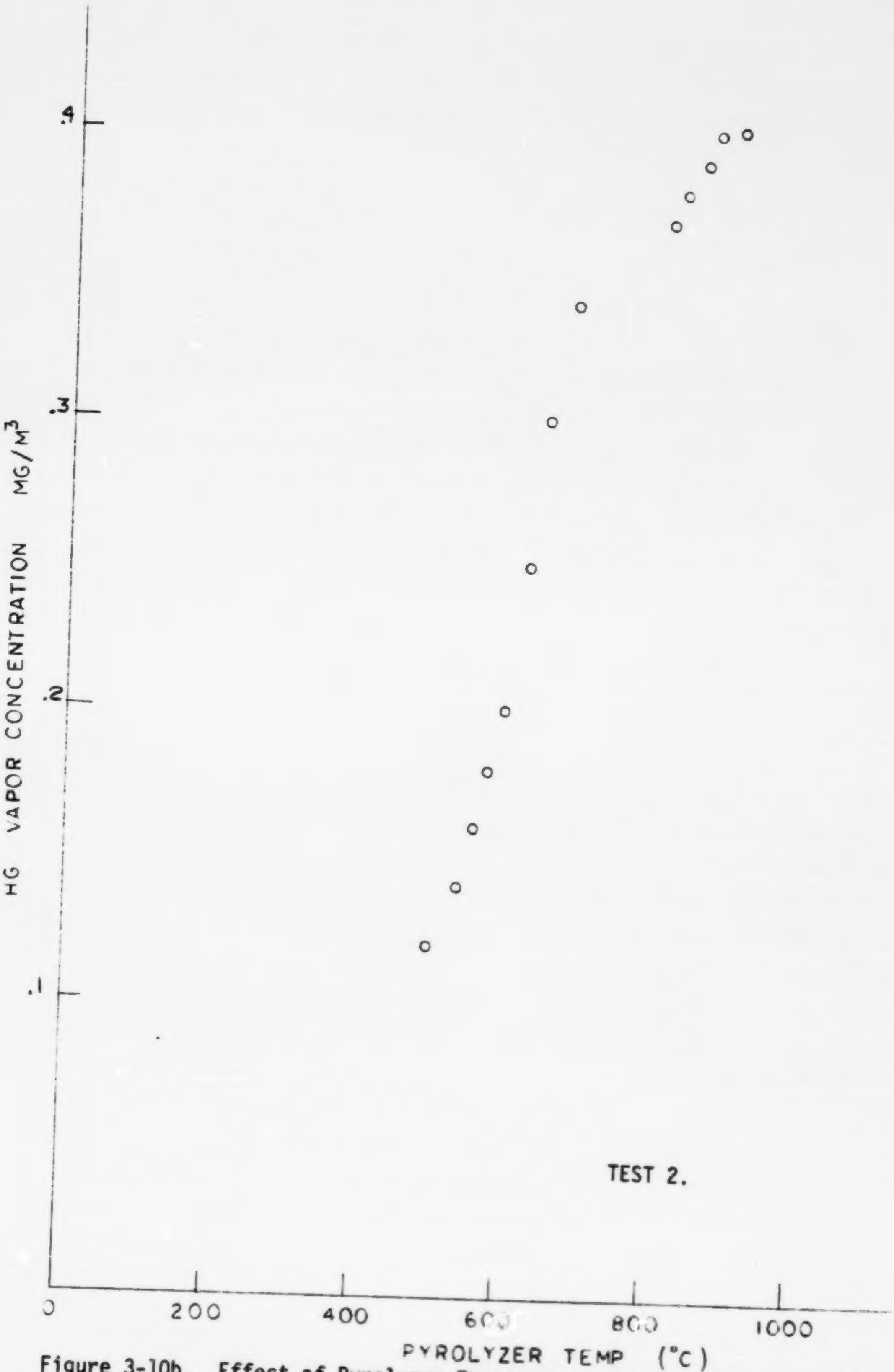


Figure 3-10b. Effect of Pyrolyzer Temperature in the Decomposition of Mercuric Chloride Aerosol.

necessary. At operating temperatures of nearly 500°C, they found many mercury compounds, including mercuric chloride, decomposed without catalyst. The Geomet converter will be employed in the field at an operating temperature of 600°C.

4. Sulfur Dioxide Removal

Laboratory tests were performed to determine the efficiency of various systems for removing SO_2. The test apparatus is shown in Figure 3-11. A mixture of five percent sulfur dioxide was passed through a series of impingers containing a scrubbing solution at the volumetric flow rate of one liter per minute. The scrubbed gas was then analyzed by a Dynasciences sulfur dioxide monitor (SS-330) to determine the efficiency of various scrubbing solutions. Also, a packed tube was used to test the absorption of sulfur dioxide by various solids. It was found that both sodium carbonate and hydrogen peroxide completely removed sulfur dioxide; however, sodium carbonate removed sulfur dioxide to its theoretical limit whereas hydrogen peroxide did not. None of the solid absorbents were found effective in the removal of sulfur dioxide.

Three midget impingers were added to the mercury generating system in the mercury stream as shown in Figure 3-12. Several tests were run with varying solutions of sodium carbonate added to the impingers. The Beckman was used as the monitoring instrument. The mercury stream was alternated at three minute intervals for a thirty minute period through the impingers and bypass. No significant change in instrument readings occurred during these shifts, although minor fluctuations were observed due to variations in flow. Calculations of the mercury flow consistently agreed with the instrument readout. Five percent sulfur dioxide was added to the mercury stream while bubbling through the sodium carbonate and again no change in the mercury concentration occurred. Varying concentrations of sodium carbonate were used in the impinger solutions with all samples indicating complete removal. Sulfur dioxide and mercury were bubbled through one sample until all the sodium carbonate was completely reacted. Upon depletion of the sodium carbonate, the instrument readout immediately rose above scale and remained there. Each test run indicated sodium carbonate would totally scrub out sulfur dioxide with no removal of mercury.

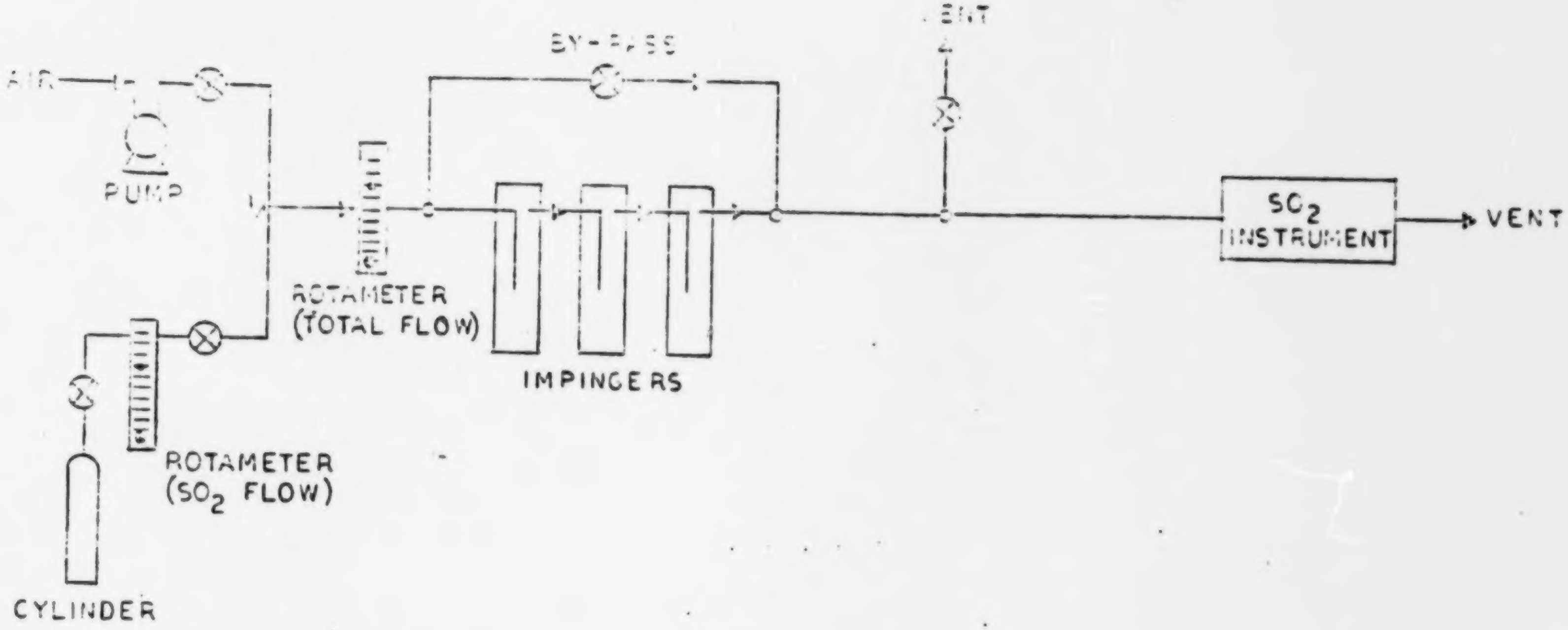

AIR
PUMP
BY-PASS
VENT
ROTAMETER (TOTAL FLOW)
IMPINGERS
SO_2 INSTRUMENT
VENT
ROTAMETER (SO_2 FLOW)
CYLINDER

Figure 3-11. Sulfur Dioxide Removal System.

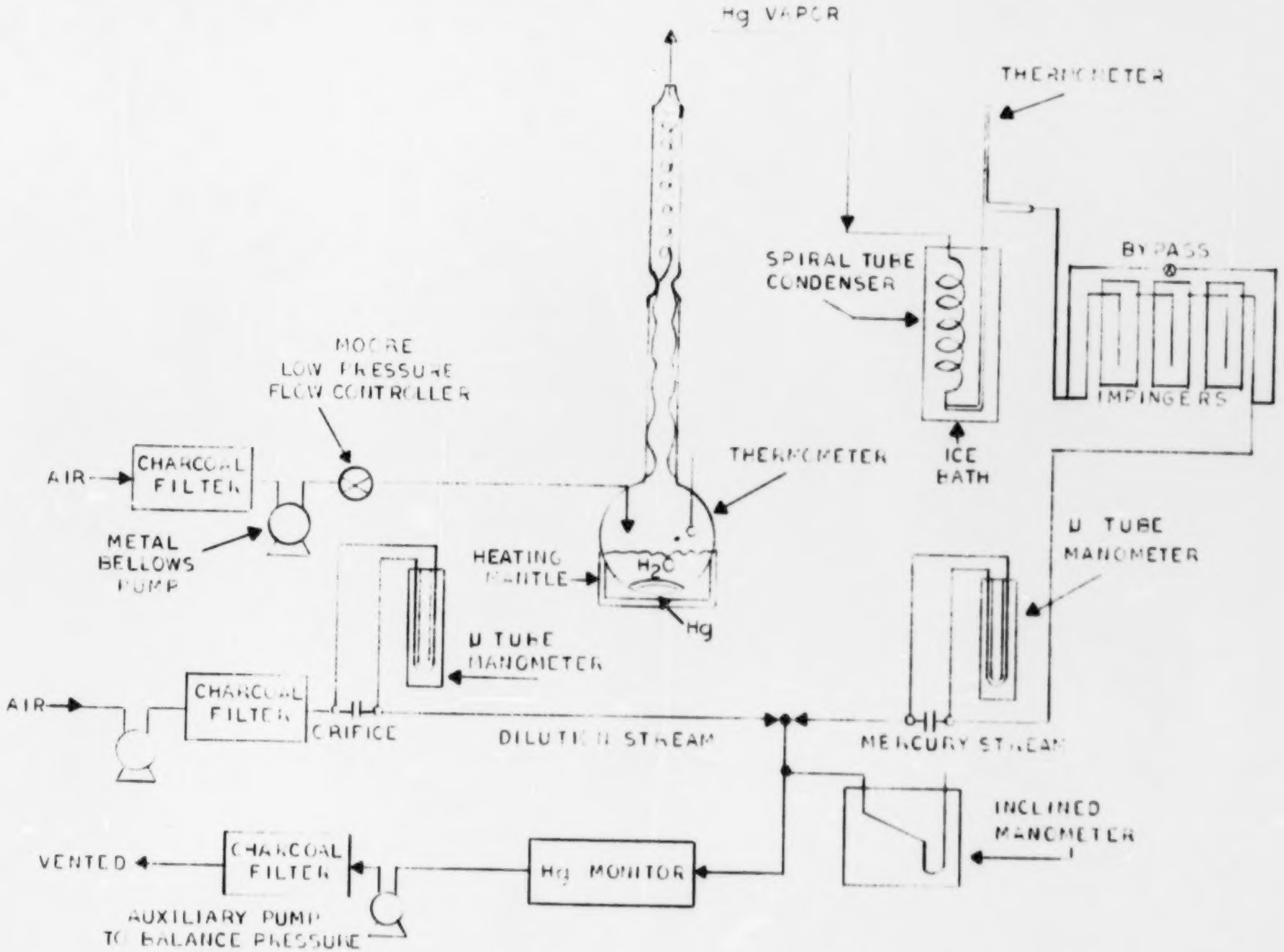

Hg VAPOR
THERMOMETER
SPIRAL TUBE CONDENSER
BYPASS
IMPINGERS
MOORE LOW PRESSURE FLOW CONTROLLER
THERMOMETER
ICE BATH
AIR
CHARCOAL FILTER
METAL BELLOWS PUMP
HEATING MANTLE
H_2O
Hg
U TUBE MANOMETER
U TUBE MANOMETER
AIR
CHARCOAL FILTER
ORIFICE
DILUTION STREAM
MERCURY STREAM
INCLINED MANOMETER
VENTED
CHARCOAL FILTER
Hg MONITOR
AUXILIARY PUMP TO BALANCE PRESSURE

Figure 3-12. Mercury Generating System with Sulfur Dioxide Removal.

Similar tests were performed with hydrogen peroxide as the scrubbing agent. Hydrogen peroxide solutions indicated not only complete removal of sulfur dioxide but also substantial removal of mercury. As the peroxide reacted with the sulfur dioxide, the instrument concentration would drop until the level approached zero. It was concluded that sodium carbonate would serve as an adequate scrubbing solution for use in the field system.

The effective interference of sulfur dioxide on the instruments was observed by introducing known quantities of the gas into each monitor. The equivalent mercury levels were recorded and the results are shown in Table 3-3. The Dupont and Olin indicated the largest interference and the Beckman and Sunshine showed less response to the sample gas. The Dupont and Olin were operated lacking the optical filters capable of cancelling sulfur dioxide interference. During the field study at the zinc smelter, the Dupont was equipped with this filter as the sulfur dioxide levels were quite high.

TABLE 3-3

SULFUR DIOXIDE INTERFERENCE

mg/m^3 SO_2	Volumetric Flow (cc/min)	Beckman (mg/m^3)	Dupont (mg/m^3)	Sunshine (mg/m^3)	Olin (mg/m^3)
1,290	2,030	0.027	0.13	0.04	0.10
1,600	2,030	0.036	0.27	0.08	0.25
5,710	2,030	0.068	0.44	0.18	0.39
1,430	550	0.032	0.19	0.04	0.12
5,710	550	0.070	0.41	0.15	0.34

C. ZERO AND SPAN STABILITY

Determination of span and zero drift was made during both the laboratory tests and also in the field. Zero gas was passed into the Beckman, Sunshine, Dupont, and Olin with the outputs of the instruments recorded at various intervals of time. Throughout these periods of time, mercury was intermittently passed through the instruments with a return to zero air prior to any zero measurement. Table 3-4 shows the indicated instrument readings versus the hours of operation.

TABLE 3-4

ZERO DRIFT MEASUREMENTS

Time (hr)	Beckman (mg/m^3)	Sunshine (mg/m^3)	Dupont (mg/m^3)	Olin (mg/m^3)
0.5	0	0.03	0	0
1.0	0	0.04	0	0
1.5	0	0.06	0	0.01
2.0	0	0.07	0	0.01
2.5	0	0.07	0	0.02
3.0	0	0.06	0	0.01
3.5	0.01	0.07	0	0.01
4.0	0.01	0.08	0	0.01
8.0	0.005	0.09	0	0.01
12.0	0.012	0.09	0.05	0.01
24.0	0.015	0.08	0.03	0
68.0	0.02	Needle pinned below zero	0.02	0.02
88.0	0.015	Needle pinned below zero	0.02	0.02
96.0			0.03	0.04
120.0			0.05	0.03

The maximum deviation from zero for the Beckman was 0.02 mg/m^3 (0-0.1 mg/m^3 range) after sixty-eight hours of operation. The Beckman, not being a continuous monitor, maintained an excellent zero through short intervals of time (eight hours or less). The maximum deviation from zero for the Sunshine was 0.09 mg/m^3 (0-1 mg/m^3 range) after only eight hours. The Sunshine never maintained a steady zero and continually drifted up and down scale after short periods of time (one hour or less). The maximum deviation from zero for the Dupont was 0.05 mg/m^3 (0-1 mg/m^3 range) after twelve hours. The Dupont showed no detectable zero drift for up to twelve hours and maintained extremely good stability throughout the program. The maximum deviation from zero for the Olin was 0.04 mg/m^3 (0-1 mg/m^3 range) after ninety-six hours. The Olin drifted only slightly through eighty hours, and as did the Dupont, also indicated unusually good stability.

The span drift was observed with the use of the calibration filters contained in each instrument. The span drift was not quantitatively noted; however, qualitative assessments were based on laboratory and field experience. The span stability for the Olin, Dupont, and Beckman was quite precise as corrections in span adjustment were seldom required. The Sunshine required span adjustments at frequent intervals which might be accountable to the special calibration system installed at the Walden laboratory. The Geomet was tested for zero from time to time, generally each of many times we encountered difficulties with the applicability of the instrument. However, throughout our use of the instrument, approximately one hundred and forty hours, no zero drift was observed. We were unable to test the span drift of the Geomet. No stability tests were run with the tape stain sampler.

D. RESPONSE TIME

The response time of the instruments was observed in the laboratory. The time interval from a change in mercury concentration to the time the final value is displayed on the measuring device of the instruments was interpreted as response time. The dead time of the sample lines and flow metering components of the laboratory setup was negligible with respect to instrument lag. The Olin, Sunshine, and Beckman responded quite similarly in the laboratory with the Sunshine responding the most quickly. The response time of these three instruments varied from fifteen seconds to approximately forty-five seconds depending on the flow rate of the mercury stream. The response time of the Dupont was somewhat slower due to the twenty inch cell used in the laboratory. It ranged from about twenty-five seconds to one minute. The Dupont's response time was not observed with the two inch cell installed.

The response time of the instruments in the field increased due to sampling system dead-time as they were located some distance from the mercury source, particularly at the red oxide of mercury facility and the zinc smelter. The response time exceeded three minutes at the end box testing with only the Olin monitor. This was due to the need for locating the Olin monitor, considering its size, out of the cell room. In this instance, the response time of the Olin ran as much as four minutes. The response time of the Geomet was dependent on the timing cycle desired for storing the mercury sample on the silver grids. For all applications in this program, the timer was adjusted to the minimum cycle of two minutes.

E. SENSITIVITY

The sensitivity of the monitoring instruments was interpreted as the minimum detectable instrument response. The Beckman, Dupont, and Olin provide range selection for a measuring scale of 0-0.1 milligram per cubic meter, whereas the Sunshine is designed with only a 0-1.0 milligram per cubic meter scale. The minimum detectable level of the Beckman was 0.005 milligrams per cubic meter, the Olin and Dupont was 0.01 milligrams per cubic meter, and the Sunshine was 0.02 milligrams per cubic meter. The Geomet was by far the most highly sensitive instrument evaluated, with a minimum detectable response in the range of nanograms per cubic meter. The high sensitivity of the Geomet represents a distinct disadvantage for continuously measuring high level emissions from mercury sources. None of the instruments tested are capable of measuring mercury for source emissions without the use of a dilution system. The intrinsic high sensitivity of each instrument is not necessary for the applications required by this program.

F. RELIABILITY

The reliability of each instrument was observed throughout the laboratory and field studies. The Olin was operated in the laboratory for limited periods of time and was not the same instrument tested in the field.

Neither of these instruments had any electronic failures during the program. The recorder on the field monitor required replacement of the slidewire, but remained operational throughout the testing. The Dupont was kept on almost constantly while in the laboratory and remained turned on five days a week in the field. During the field testing of the hydrogen stream, the Dupont was not operational due to a loose connection in the control station. The connection apparently loosened during the shipment and movement of the instrument. Also, the zero potentiometer on the control station needed replacement as it tended to slip upon zero adjustments. Both the Olin and Dupont had been used frequently prior to this program and had numerous operating hours.

The Beckman, Sunshine, and Geomet were relatively new instruments. The Beckman, not designed as a continuous monitor, frequently required new mercury vapor lamps. Adjustments were also necessary on the coarse sensitivity and range ratio as the front panel controls were not adequate. During the field trip to the red oxide of mercury facility, the phototubes and mercury lamp were replaced by a Beckman technical representative. The Sunshine also required replacement of the light source but not as frequently as the Beckman. While testing at the end box vent of the chlor-alkali plant, the Sunshine stopped responding to mercury. Replacement of the mercury light source did not alter this situation and only after considerable efforts was the instrument made operational. The exact cause was never resolved although from that point on, the Sunshine could not be left on continuously without the meter readings dropping to zero. The Geomet remained in good working order throughout its use in the field while in the laboratory the grid had to be replaced. While attempting to zero the Geomet with air scrubbed in iodine monochloride, moisture entered the grid and shorted the grid wires. A replacement grid was sent immediately and remained in operation through the remainder of the program.

G. RELATIVE ACCURACY AND PRECISION

The relative accuracy and precision of the Beckman, Olin, Sunshine, and Dupont with both the twenty inch and two inch cell was determined by testing the monitors separately in conjunction with the mercury generating system. Each instrument was operated for a conditioning period of at least four hours prior to the performance tests. Instrument calibrations were carried out before each series of tests while as many as twelve test series were performed on each instrument. No more than fifteen separate sample points were taken in each series so that the operation of the monitors would somewhat simulate the day to day monitoring anticipated in the field. The calculated concentrations of the generating system were recorded and compared to those of the instruments. This data is shown for each instrument in Table 3-5 through Table 3-9, see Appendix A.

The relative accuracy was determined by linear regression analysis of the paired data for the generating system and instrument readings. The linear regression line for each instrument was obtained and employed in the accuracy calculations. These equations and the regression lines are indicated in Figure 3-13 through Figure 3-17. The relative accuracy was defined as the correctness of the instrument relative to the value given by the reference method (mercury generating system). The relative accuracy was expressed as the instrument readings relative to concentrations of 0.30, 0.60, and 0.90 milligrams per cubic meter of mercury (30, 60, and 90 percent of full scale) as calculated from the generating system. The relative accuracy of the instruments is shown in Table 3-10. The information in Table 3-10, in itself, does not provide a completely clear picture of the accuracy. The correlation coefficient, a statistic that measures the strength of the linear relationship between the two variables, further assists in developing a total statement on the accuracy of the instruments.

The Beckman was very accurate for a portable monitor with an extremely high correlation coefficient of 0.980. The Dupont, tested with the twenty inch cell, was quite inaccurate, however, it should be noted that the correlation coefficient was quite high at 0.986. The Dupont, tested with the two inch cell, also was relatively inaccurate but showed a high correlation coefficient of 0.988. The major causes of the inaccuracy were directly related to the cell length and manufacturer's calibration data. In using a twenty inch cell, the Dupont was incapable of maintaining

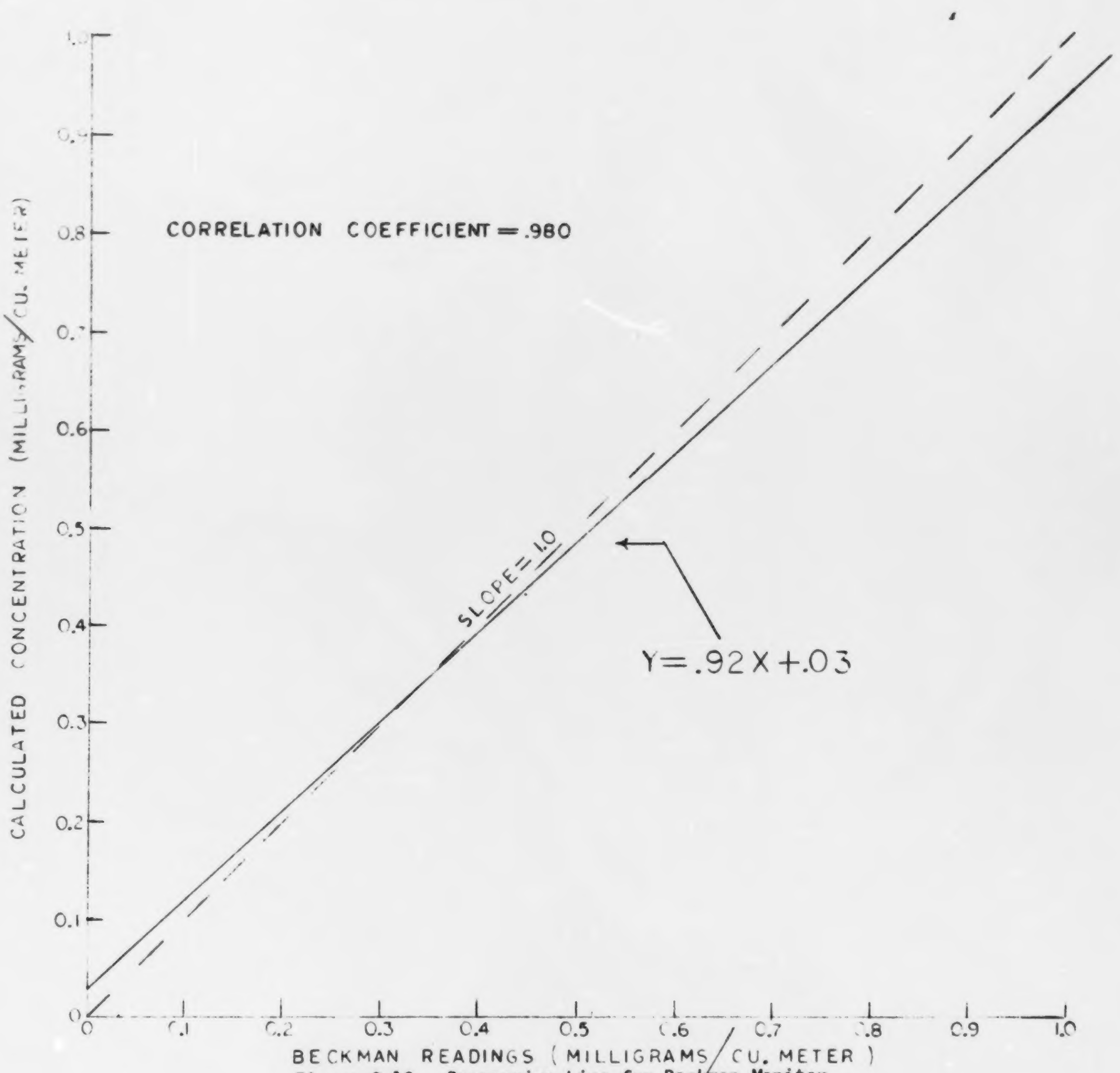


Figure 3-13. Regression Line for Beckman Monitor.

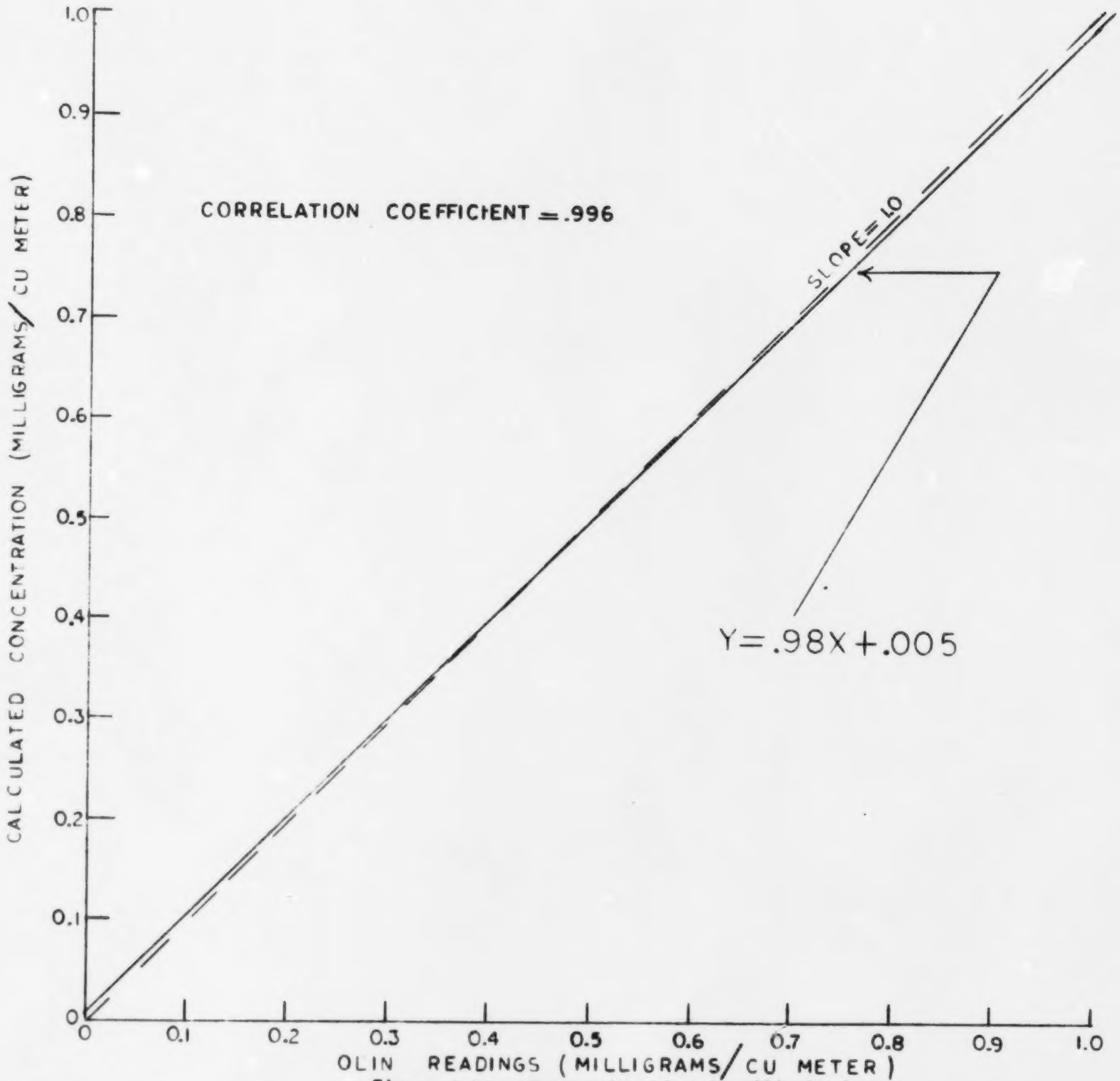


Figure 3-14. Regression Line for Olin Monitor.

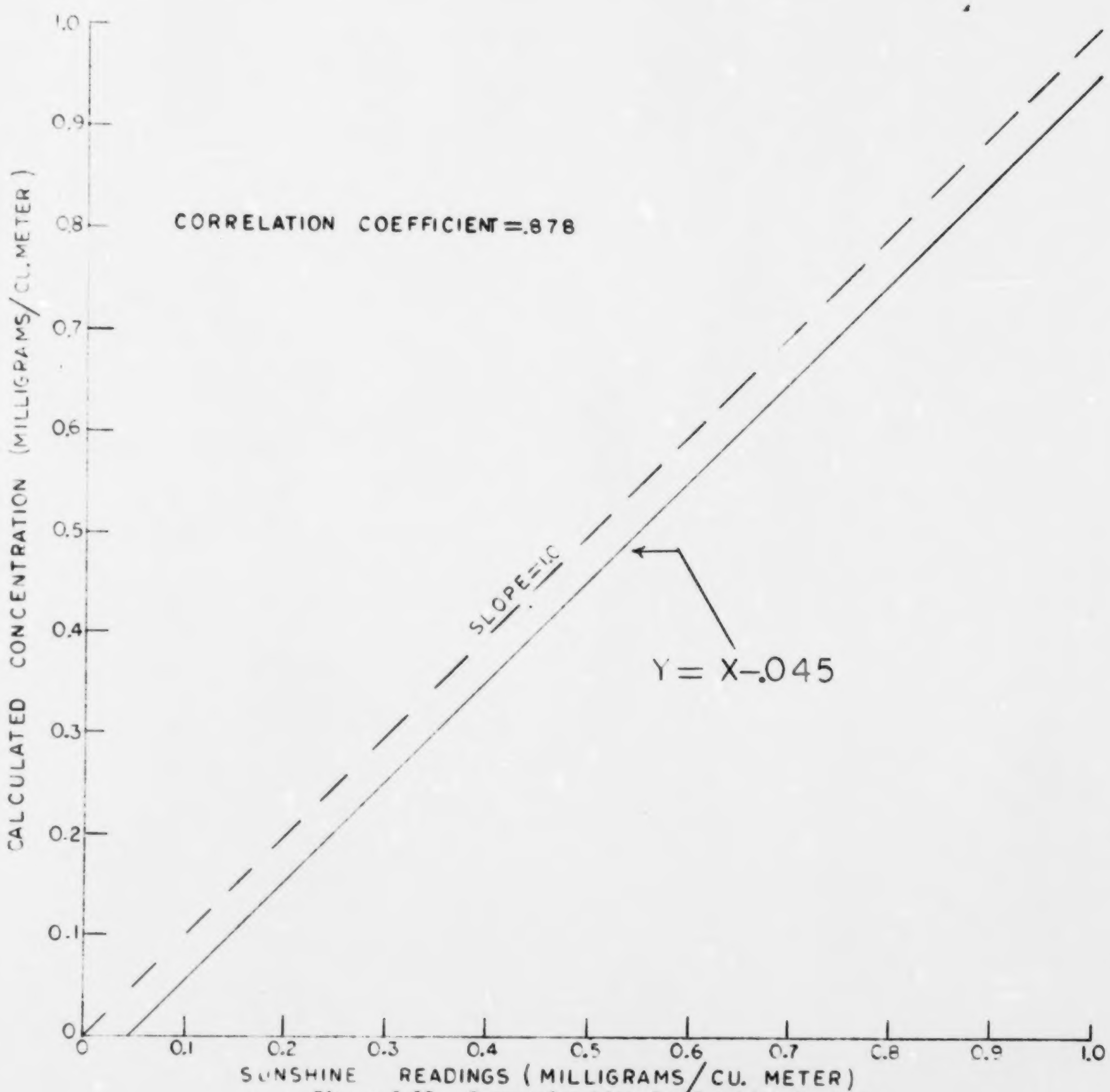


Figure 3-15. Regression Line for Sunshine Monitor.

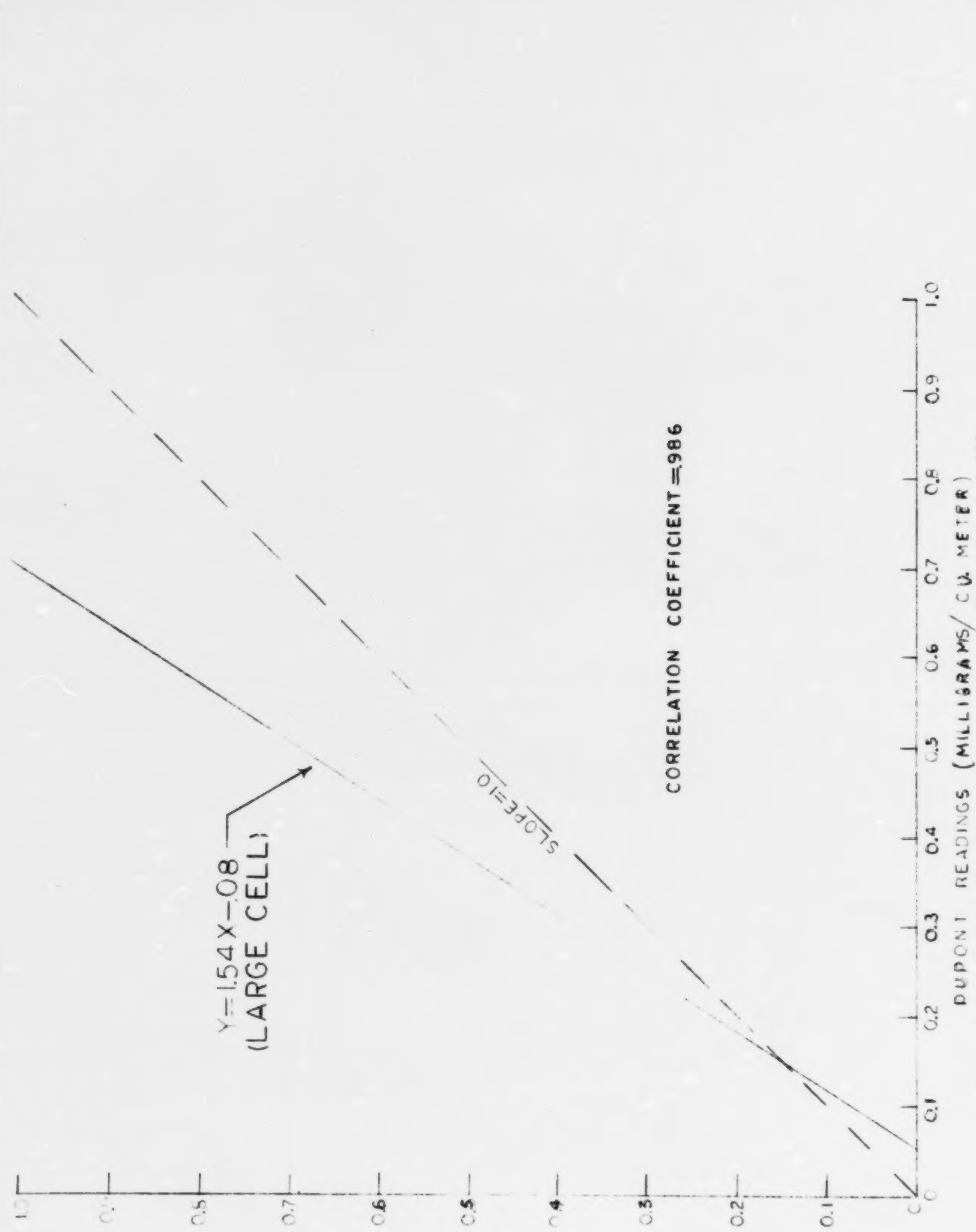


Figure 3-16. Regression Line for Dupont Monitor (Twenty Inch Cell)

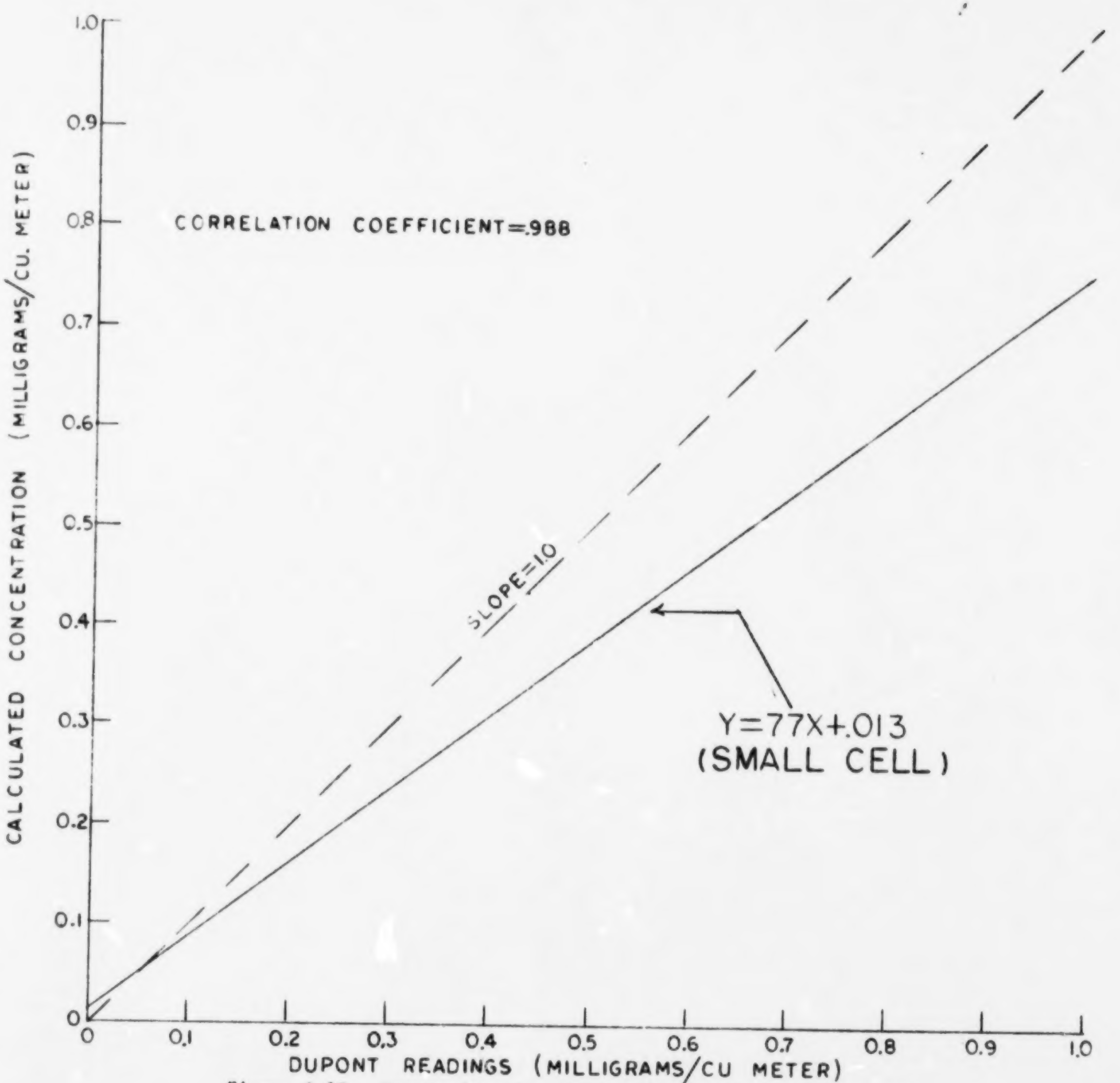


Figure 3-17. Regression Line for Dupont Monitor (Two Inch Cell).

TABLE 3-10

RELATIVE ACCURACY OF INSTRUMENTS

	Generating System Concentration		
	0.30 mg/m^3	0.60 mg/m^3	0.90 mg/m^3
Instrument Variation (% of full scale)			
Beckman	97%	103%	106%
Olin	100%	102%	101%
Sunshine	115%	108%	105%
Dupont (20" cell)	83%	73%	71%
Dupont (2" cell)	123%	127%	128%

linearity. Applying Beer's Law, at high concentrations with a twenty inch cell, the log amplifier is extended beyond its linear range.

The Olin was the most accurate instrument with almost no deviation from the reference method. The correlation coefficient was 0.996. The Sunshine appeared to be quite accurate applying the regression analysis, however, the correlation coefficient was extremely low, 0.878, compared to the other instruments.

The precision was defined as the standard error of the mean, in terms of the quantity being measured, as plus or minus so many milligrams per cubic meter of mercury. It is derived from the following equations:

$$r^2 = 1 - \frac{Se^2}{Sy^2}$$

and

$$Sy^2 = \frac{1}{n} \sum (y-\overline{y})^2$$

where the quantity r is the correlation coefficient, Se is the standard error of the mean, Sy^2 is the error variance, n is the number of sample points, y is the value of the standard concentration, and $\overline{y}$ is the mean of those values. From these two equations, the standard error is found to equal the following:

$$Se = \sqrt{(1-r^2)(Sy^2)}$$

The correlation coefficients and error variances were determined by linear regression analysis of the data for the generating system and each instrument. The precision of each instrument is given in Table 3-11.

TABLE 3-11

PRECISION OF INSTRUMENTS

Instrument	Precision
Beckman	± 0.052 mg/m^3
Olin	± 0.027 mg/m^3
Sunshine	± 0.109 mg/m^3
Dupont (20" cell)	± 0.028 mg/m^3
Dupont (2" cell)	± 0.040 mg/m^3

As might be expected, the precision of the Olin and Dupont are in good agreement as they both employ the same analyzer. Their level of precision appears adequate for use as a continuous monitor. The precision of the Beckman is exceptionally high for a portable monitor, indicative of the overall performance of the Beckman. The precision of the Sunshine was considerably less than the other instruments.

Summarizing, the Olin performed well within any accuracy requirements for a continuous monitor. The Beckman also performed with high accuracy, but cannot be employed in its present configuration as a continuous monitor. The Dupont, with a twenty inch cell, is not an accurate instrument for source monitoring even though the electronic accuracy of the instrument is confirmed by the results of the Olin tests. Tested with a two inch cell, the Dupont again did not perform well due to calibration errors.

Nevertheless, these problems are associated with instrument application and not the direct electronic performance of the instrument. As shown by the Olin, the proper application and standardization of the Dupont will result in a highly accurate instrument.

IV. RESULTS OBTAINED IN THE FIELD

A. FIELD SAMPLING SYSTEM

The original field sampling system is shown in Figure 4-1. The system consisted of an EPA sampling train for mercury emissions (40 CFR 61:38 FR8820, April 6, 1973) and a sampling leg that contained the mercury monitors. Isokinetic flow was maintained in this stream at all times, and iodine monochloride impingers were only included when referee tests were run. About one liter of gas sample was drawn from the isokinetic stream prior to the impingers. This sample stream was passed through the pyrolyzer unit (catalytic converter) to convert any gaseous and particulate mercury compounds to elemental mercury and break down all hydrocarbons. Following the pyrolyzer, the stream was split passing approximately six to ten milliliters of gas to the Geomet instrument. The main stream was pumped through a rotameter by a teflon lined pump and then diluted with clean, regulated air. Depending on the flow requirements for dilution, the instrument flow rates were maintained at approximately one liter per minute by evacuating the excess gas through a pressure-regulated flow meter. The instruments were located in parallel, each followed by a flowmeter. The evacuation stream also contained a flow meter. A sodium carbonate scrubber was added upstream of the instruments when sulfur dioxide was present in the gas stream.

B. MERCURY PROCESSING PLANT

1. Description of Red Oxide of Mercury Process

Prime virgin mercury is pumped from flasks to a holding tank and then added to a reactor. Nitric acid pumped from storage to a holdup tank, combines with the mercury in the reactor. The reactor serves to heat about two thousand pounds of mercury plus the required nitric acid to approximately 120°F for six to eight hours. The reaction occuring is exothermic and yields mercurous nitrate which is passed into any of three vats positioned above the three furnaces. The mercurous nitrate is added to the furnaces which have been preheated to 80°F and three additional

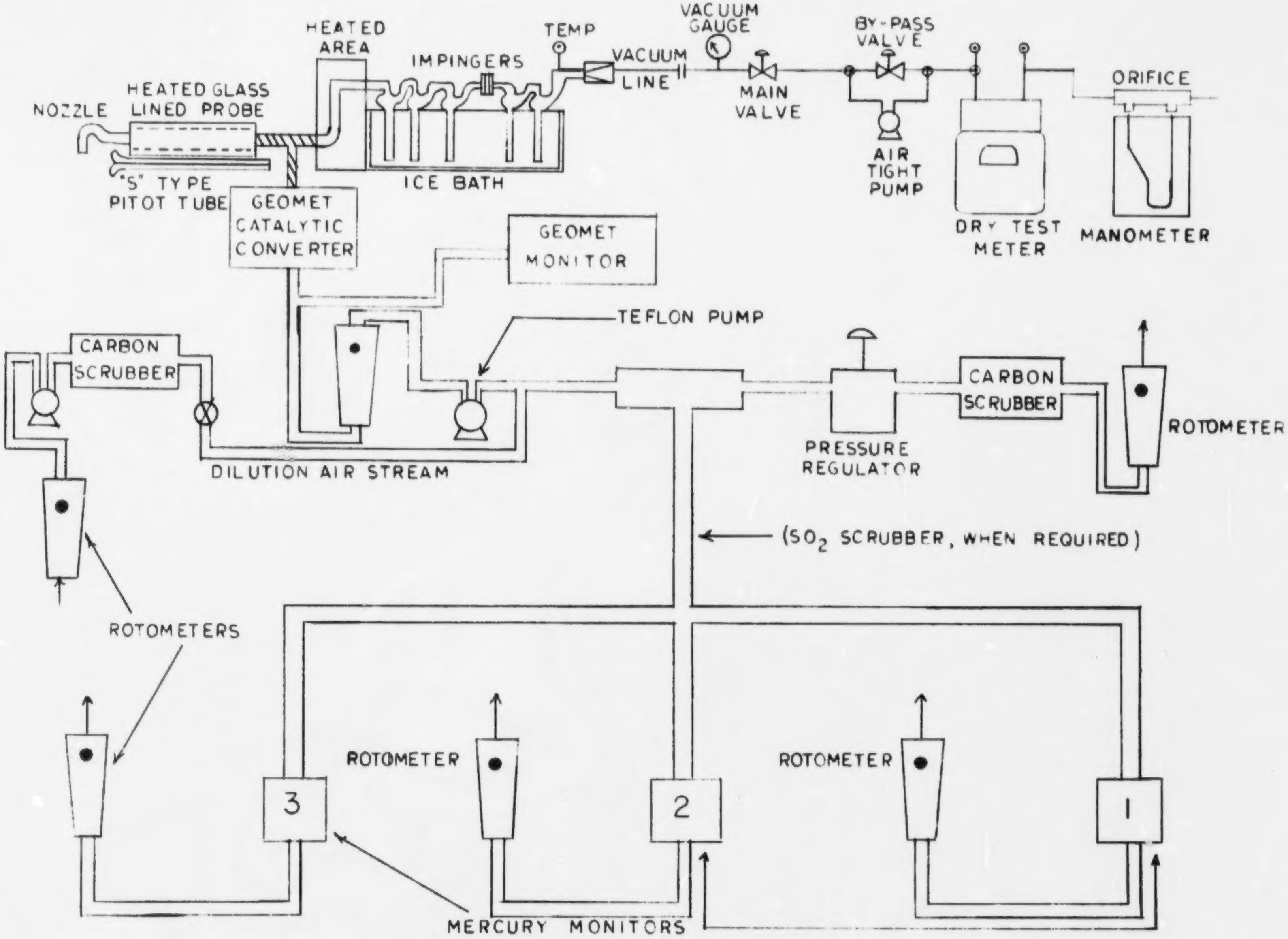

NOZZLE
HEATED GLASS LINED PROBE
"S" TYPE PITOT TUBE
HEATED AREA
IMPINGERS
ICE BATH
TEMP
VACUUM LINE
VACUUM GAUGE
MAIN VALVE
BY-PASS VALVE
AIR TIGHT PUMP
DRY TEST METER
ORIFICE
MANOMETER
GEOMET CATALYTIC CONVERTER
GEOMET MONITOR
TEFLON PUMP
CARBON SCRUBBER
DILUTION AIR STREAM
PRESSURE REGULATOR
CARBON SCRUBBER
ROTOMETER
(SO2 SCRUBBER, WHEN REQUIRED)
ROTOMETERS
ROTOMETER
ROTOMETER
3
2
1
MERCURY MONITORS

Figure 4-1. Field Sampling System

flasks of mercury are poured into each furnace operating. Increasing the furnace temperature to 120-150°F for two hours, mercuric nitrate is formed. The furnace temperature is increased to 280°F for two hours to initiate the conversion of mecuric nitrate to mecuric oxide and gradually increasing the temperature to 590-600°F for six to eight hours, the reaction is run to completion.

Furnace fumes are vented with the spillover of liquid into a mother liquor storage tank. From this tank, the fumes are passed into a common six-inch duct and then into two low efficiency wetted towers. The gases are vented to the atmosphere.

Sampling for total mercury emissions was accomplished by introducing the sample probe into the six inch vent line through a three inch test port at the location shown in Figure 4-2. The test point was located at the midpoint of the vent. The test site was chosen so that the equipment could be operated within the building.

2. Test Results

The tests at the red oxide facility were conducted from April 10, 1973 to April 25, 1973. Data were taken every five minutes while the sampling system was in operation. This data is shown in Table 4-1, (see Appendix A). The pyrolyzer temperature was set at 600°C and the heated teflon tubing temperature was adjusted for 200°C. The instruments tested at this site were the Beckman, Sunshine, and Dupont. The Dupont was left running continuously whereas the Beckman and Sunshine were operated only ten hours per day. Instrument calibrations were performed twice a day except during zero drift tests.

No data was obtained on April 10 and April 11 as both days were required for system set-up.

Initially, the Beckman and Sunshine could not be zeroed. The zero air was produced by pumping ambient air through carbon scrubbers and, later in the tests, through three impingers of iodine monochloride with

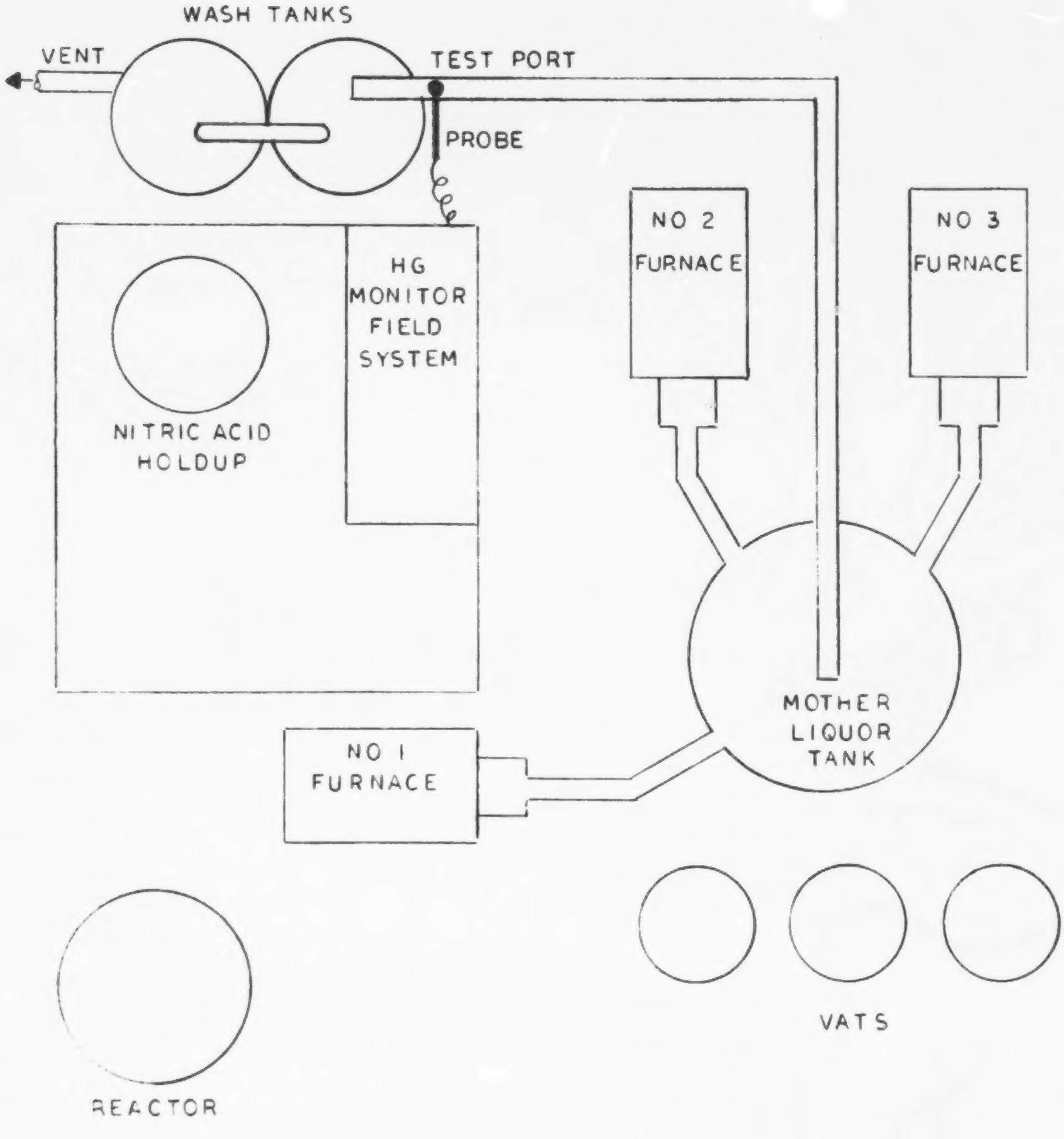

WASH TANKS
VENT
TEST PORT
PROBE
NO 2 FURNACE
NO 3 FURNACE
HG MONITOR FIELD SYSTEM
NITRIC ACID HOLDUP
MOTHER LIQUOR TANK
NO 1 FURNACE
VATS
REACTOR

Figure 4-2. Red Oxide of Mercury Facility.

silica gel. It was deduced that nitrogen oxides from the process emissions were present and not being scrubbed out. The single wave-length instruments were apparently affected by the interference of nitrogen oxides. The Dupont dual wavelength scheme appeared to show no effects due to the interferences.

Finally, a cylinder of zero test air was purchased for use as a zero standard and dilution air source replacing the on-site generated source. Preliminary tests were carried out, but no useful data were obtained. All three furnaces shut down in mid-afternoon at which time laboratory work was initiated for iodine monochloride testing.

On April 17, data was obtained while one furnace was in operation, until the Beckman instrument failed, at which point the test was terminated. The Beckman unit could not be repaired at the test site and arrangements were made to transport the instrument to the local service representative.

Four reference tests were taken during the field testing at the mercury processing plant. A quarter-inch stainless-steel nozzle was employed at the probe inlet for all four tests. During each reference test the instrument meter readings and flow rates were taken every five minutes and then averaged over the total test time. The necessary flow rates, temperatures, pressures and other data, and laboratory measured and analyzed parameters were recorded and used to calculate the mercury concentrations in the reference samples. Comparison of the reference tests and the instrument measurements are shown in Table 4-2. The analyses were performed in the Walden laboratory on a Heath Model 703 Spectrophotometer by Walden personnel. The method of analysis was the procedure described in the Federal Register, April 6, 1973.

During tests 1 and 2, a dark purplish precipitate formed in the second impinger. Also the silica gel was tinted to the color of iodine indicating possible carryover of some iodine monochloride. The sample recovery procedure was modified so as to dissolve the precipitate into solution for

TABLE 4-2

COMPARISON OF REFERENCE TESTS AND INSTRUMENTS MEASUREMENTS

Test No.	Date	Time	Reference Test (ICL) mg/m^3 Hg	No. of Furnaces Operating	Dupont* mg/m^3 Hg	Beckman* mg/m^3 Hg	Sunshine* mg/m^3 Hg
1	4/18	10:00-11:30 am	11.4	2	0.04		0.37
2	4/20	3:00-4:00 pm	295.45	3	0.15	0.18	0.06
3*	4/23	11:00-12:00 am	3.97	2	0.97	2.42	
4*	4/24	11:25-11:25 am	1.05	1	0.54	0.93	0.69

---

*The instrument concentrations were determined by multiplying the instrument meter readings by the dilution ratio when the dilution system was operating.

analysis. All AA analyses were run upon completion of testing at this field site. The unusually low levels of mercury recorded by the instruments during test 1 and 2 appeared suspicious. As the results later indicated, the sampling system was not transporting a representative sample to the instruments.

The sampling system was modified prior to obtaining the third iodine monochloride test. The instrument sampling line was disconnected from the EPA train and a separate quarter-inch teflon nozzle was placed on the inlet of the effluent stream. The Teflon nozzle was attached in the stack adjacent to the EPA probe. As can be noted from the data in Table 4-2, the mercury levels in the instrument stream increased significantly in tests 3 and 4. During these tests, the agreement between the reference tests and the instrument stream concentrations was much better than that of the first two tests. No precipitate was found in the impingers following the completion of the third and fourth tests. Although this sampling scheme produced closer agreement between instrument readings and reference test results, this method precluded sampling isokinetically through the instrument stream.

On April 25, preparations for a fifth iodine monochloride test were interrupted by a nitric acid spill. A flange, located above the test area, burst, spraying nitric acid over the equipment and surrounding area. The remainder of the day was spent on cleaning the equipment and determining the extent of damage. It was decided to return to the Walden laboratory to fully evaluate the extent of damage and effect appropriate repairs. The result of this accident was a two-week delay. Fortunately, no internal damage was incurred in any instrumentation although the external features of much of the equipment was harmed.

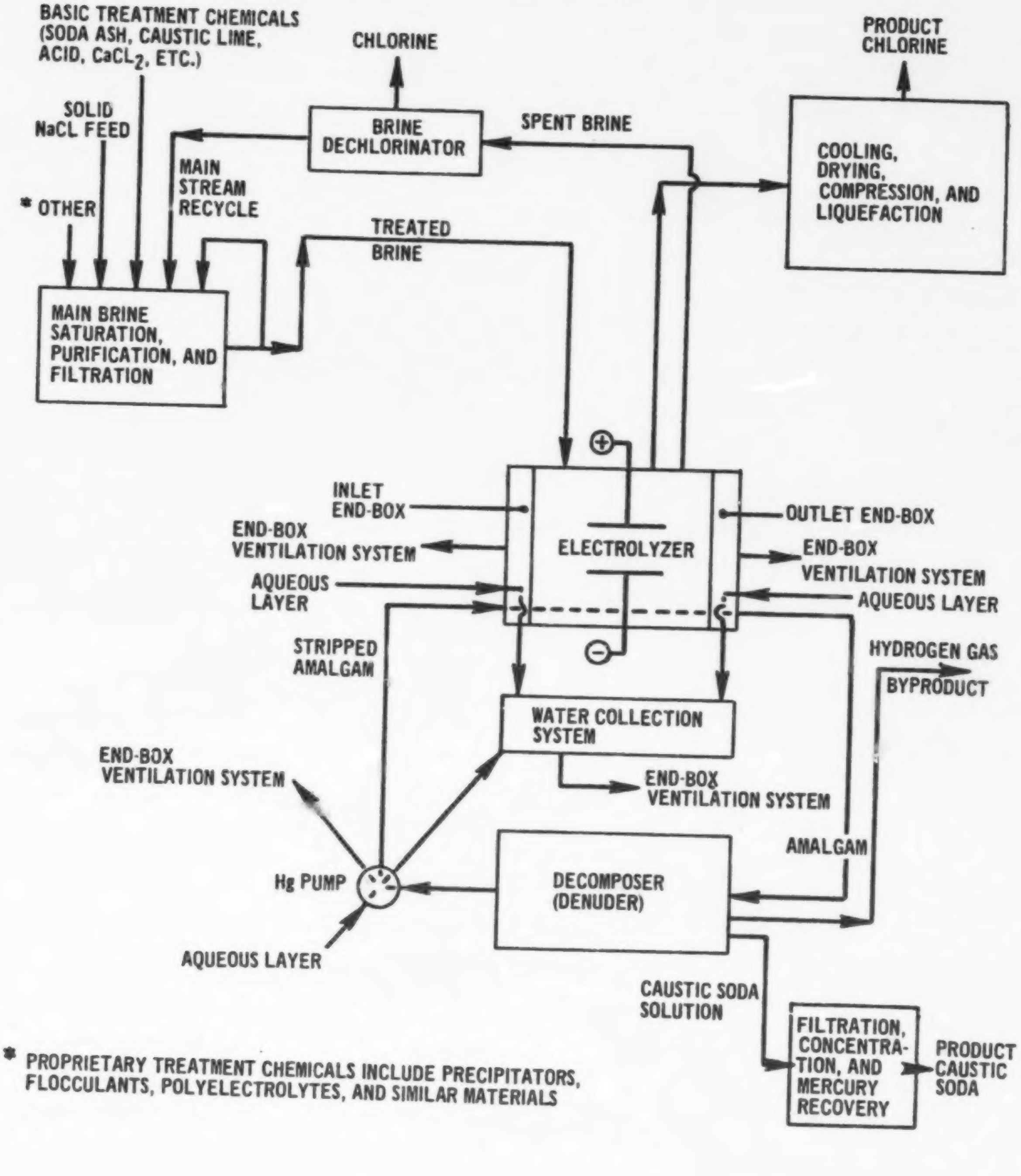
The field program was developed with the intention that the testing at the first site would serve mainly to establish the integrity of the sampling system and testing methods as well as gathering performance data. Our aim was to modify any aspects of the system as opposed to generating extensive data as the main source of data was planned to be a chlor-alkali plant. In this respect, the field testing at the red oxide of mercury facility did serve the intended ends. The third and fourth tests indicated a major improvement in the sampling system as the instrument readings compared fairly well with the reference test results. The Beckman monitor showed close agreement with the fourth reference test and the sampling system appeared to be operating more effectively than at first.

It was also found that the heated Teflon tubing appeared to evolve mercury for extensive periods of time before instrument zeroing could be achieved. The heating unit was shut off and consequently the instruments zeroed quite rapidly.

C. CHLOR-ALKALI PLANT

1. Description of Chlor-Alkali Process

The following process description is substantially extracted from Reference [5]. In this process, schematically shown in Figure 4-3, purified and nearly saturated brine is fed continuously through the inlet end-box to the electrolyzer where it flows between a stationary graphite anode and a flowing mercury cathode. The inlet end-box provides a connection for the feed brine and the stripped mercury as it returns from the decomposer and also serves to keep the incoming mercury covered with brine. The chlorine gas formed at the anode is discharged from the electrolyzer for further treatment. The sodium amalgam flows from the electrolyzer through the outlet end-box to the decomposer where it acts as the anode to a short-circuited graphite cathode in an electrolyte of sodium hydroxide solution. The outlet end-box is placed on the outlet of the electrolyzer to keep the sodium amalgam covered with spent brine and physically separate these two streams. Purified water is fed continuously to the decomposer and reacts with the sodium amalgam. The products of this reaction are sodium hydroxide solution and hydrogen gas. The caustic soda is of high purity and leaves the decomposer at a concentration of about 50 percent by weight. At the test site, the by-product hydrogen gas, which saturated with mercury corresponding to the temperature, is burned in a waste-heat boiler.


BASIC TREATMENT CHEMICALS (SODA ASH, CAUSTIC LIME, ACID, $CaCL_2$, ETC.)
CHLORINE
PRODUCT CHLORINE
SOLID NaCL FEED
BRINE DECHLORINATOR
SPENT BRINE
* OTHER
MAIN STREAM RECYCLE
COOLING, DRYING, COMPRESSION, AND LIQUEFACTION
TREATED BRINE
MAIN BRINE SATURATION, PURIFICATION, AND FILTRATION
+
INLET END-BOX
OUTLET END-BOX
END-BOX VENTILATION SYSTEM
ELECTROLYZER
END-BOX VENTILATION SYSTEM
AQUEOUS LAYER
AQUEOUS LAYER
−
STRIPPED AMALGAM
HYDROGEN GAS BYPRODUCT
WATER COLLECTION SYSTEM
END-BOX VENTILATION SYSTEM
END-BOX VENTILATION SYSTEM
AMALGAM
Hg PUMP
DECOMPOSER (DENUDER)
AQUEOUS LAYER
CAUSTIC SODA SOLUTION
FILTRATION, CONCENTRATION, AND MERCURY RECOVERY
PRODUCT CAUSTIC SODA

* PROPRIETARY TREATMENT CHEMICALS INCLUDE PRECIPITATORS, FLOCCULANTS, POLYELECTROLYTES, AND SIMILAR MATERIALS

Figure 4-3. Schematic of the Chlor-Alkali Process

Sampling for total mercury emissions was performed at two locations in the chlor-alkali process. Testing at the end-box vent was accomplished by introducing the sample probe and Teflon line into the eight-inch vent line through a three-inch hole. The stack was located adjacent to the cell room, therefore, the instrumentation was situated in the building while the EPA mercury train was located outside of the cell room. Testing of the hydrogen stream was accomplished by attaching quarter-inch Teflon tubing to a valve outlet of the hydrogen stream to the boiler burners. Although this stream does not emit directly to the atmosphere, as required by EPA testing regulations, the importance of testing in a hydrogen stream warranted this exception. Verbal approval was granted by the Program Manager.

2. Test Results at the End-Box Vent

The end-box vent stack was tested from May 15, 1973 through May 25, 1973. The Beckman, Dupont, Olin, Geomet, and Sunshine monitors were tested at this site. The Olin unit was provided by the plant as they employed the instrument for monitoring air quality in the cell room. The Olin instrument was modified to provide a range of 0 to 2.0 milligrams per cubic meters by inserting the same cell that was calibrated in the laboratory program. The stannous chloride scrubber was also operated throughout the test period. Instrument readings were recorded every five minutes except for the Geomet unit whose readings were recorded every two and one-half minutes and then averaged for five-minute intervals. The data obtained from this site is shown in Table 4-3, see Appendix A.

Due to the strong magnetic field within the cell room, the meters for the Beckman and Sunshine unit had to be shielded with Mu metal. Representatives from Geomet arrived on May 16 to assist in the preparation of their instrument for monitoring. A newly-calibrated grid was inserted in the instrument and additional silver-coated pellets were added to the dilution kit. The plant was shut down on May 16 for repairs which provided ample time for system checks and laboratory preparations. The AA analyses were performed on a Perkin-Elmer spectrophotometer provided by the plant. Plant personnel, experienced in mercury analysis, completed each analysis within one day of testing.

Initially, the Geomet unit was unable to achieve a true instrument zero. Therefore, it was decided to determine the background level of mercury due to ambient air alone and then subtract that value from subsequent mercury readings. The mercury lamp in the Beckman monitor had to be replaced to achieve acceptable instrument response.

On May 18, tests were begun to determine whether the sampling system or the instruments were the source of error in comparison to the reference tests (iodine monochloride stack samples). Midget impingers containing either iodine monochloride or potassium permanganate were placed in the exit streams of at least one of the instruments. A comparison of these samples with those tests taken directly from the stack would indicate any variation between the stack concentrations and the sample stream concentrations, assuming that no mercury is lost in the instruments. Each stream sample was run for thirty minutes. In addition, several impingers containing potassium permanganate were placed downstream of the Olin instrument (by plant personnel) to determine the stream concentration. A summary of all samples taken as this site is shown in Table 4-4, see Appendix A. It should be noted that the average instrument concentrations recorded during reference tests have been multiplied by the dilution factor for comparison with the reference test results.

The exit stream samples indicate that at least the Olin unit was adequately detecting the mercury in the sample stream. The fact that the Olin monitor was in closer agreement with the stream samples than the other instruments could be due to its stannous chloride scrubber. It was believed that the only mercury species in the end-box vent would be elemental mercury and some mercuric chloride. The pyrolyzer serves to convert the mercuric chloride to elemental mercury, however, with chlorine present, there was the likelihood of mercury recombining with chlorine to reform mercuric chloride. The stannous chloride scrubber serves to convert mercury salts, particulates, or vapors to metallic mercury and remove chlorine, thus removing any possibility of reformation of mercuric chloride. For the six stream samples analyzed, the Olin instrument averaged 88.8 percent of the AA values. The Beckman and Dupont units operated during five of the six samples and averaged 67 and 39.3 percent of the AA values, respectively. The Geomet monitor operated during three of the six samples and showed close agreement (averaged within 12 percent) with the stream samples during two of the tests while indicating poor agreement on the third test. The Sunshine unit did not operate properly during a majority of the tests due to a damaged light source and phototube.

The large differences between the reference tests and instrument readings were apparently related to sample interfacing. If particulate mercury were present in the end-box vent, the sampling system, not operating isokinetically, would not accurately represent the total mercury concentration. Yet the expected particulate mercury levels were so low that this error alone could not account for the large differences.

3. Test Results at the Hydrogen Stream

The hydrogen stream was tested from May 30 through June 6, 1973. The pyrolyzer was taken out of the system and the Geomet analyzer was not operated so as to avoid dangers associated with sparking in the presence of hydrogen. Correction charts for the flow meters were provided to convert flow rates in air to flow rates in a hydrogen atmosphere. Only the Beckman, Sunshine, and Olin units were tested as the Dupont instrument could not be made operable. Data obtained at this test site is shown in Table 4-5, (see Appendix A).

No adequate sampling probe entry ports were available on the hydrogen lines, necessitating certain modifications in the standard sampling equipment. The only available test port was a quarter-inch valve outlet prior to the boiler burners, therefore, no isokinetic reference samples were obtained. Instead, the instrument exit streams were measured for mercury by bubbling the streams through impingers containing either iodine monochloride or potassium permanganate. A total of twenty instrument stream samples were taken and a comparison of the stream concentrations with average instrument readings is presented in Table 4-6 (see Appendix A).

The Olin and Beckman instrument readings remained close throughout all hydrogen stream tests. A regression analysis on the paired average mercury concentrations for the Beckman and Olin units were derived to illustrate their relationship. The regression equation is the following:

$$Y = 0.887X + 0.078$$

with a correlation coefficient of 0.88. Y represents the average Beckman instrument readings and X the average Olin instrument readings for each test.

The information in Table 4-6 also indicates that the two absorbing solutions used in the instrument stream samples yielded significantly different results. On four occasions, iodine monochloride and potassium permanganate stream samples were taken simultaneously. Three of the four simultaneous samples indicated the mercury concentrations determined by the iodine monochloride samples to be greater than the mercury concentrations determined by the potassium permanganate samples. Also, based on the other stream samples taken, the instrument mercury concentrations were considerably lower than the iodine monochloride results, yet in close agreement with the potassium permanganate results. Apparently, iodine monochloride was absorbing non-elemental mercury species that were neither absorbed with potassium permanganate nor detected with the monitoring instruments. Lacking a pyrolyzer for conversion of mercury compounds to elemental mercury, this is quite understandable.

D. ZINC SMELTER

1. Process Description

Raw zinc ore containing approximately 30 percent sulfur by weight is roasted in two roasters, each handling approximately 300 tons of ore per day. The effluent from each roaster passes through its own collecting system and acid plant. Electrostatic precipitators remove dust and other impurities, and counter-current gas scrubbers located downstream of the precipitators also help to clean the gas. A mist precipitator removes carry-over water and some dust before the gas enters the converter.

Converted gas, after cooling, enters a packed absorbing tower. Circulating oleum is fortified by the absorption of sulfur trioxide as it passes through the tower, but it is reduced in concentration again by the addition of 98 percent acid. Product oleum is bled off continuously from the system in proportion to the amount of 98 percent acid added to the oleum system.

The gas leaving the oleum tower contains unabsorbed sulfur trioxide, and is passed to the 98 percent acid absorbing tower where absorption is completed. The effluent from this absorber and from the 98 percent absorber in the other acid plant are ducted to one common breaching and are discharged to the atmosphere through a 300 foot stack. This same stack also services the acid sintering operations. A schematic of this process is shown in Figure 4-4.

Mercury, originally present in the zinc ore, is volatilized during the roasting process and is carried through the subsequent process steps in the off-gases. Other non-ferrous smelting processes also will, similarly, generate mercury-laden effluents. In cases where no sulfur recovery process is employed, so that the effluent is vented directly to the atmosphere through tall stacks, the mercury content in the stream can be substantial. The incorporation of a sulfuric acid plant will reduce the concentration of mercury as a result of condensation and scrubbing out mercury in the last steps of the acid-making process.

In order to simulate testing at an uncontrolled smelter where an acid plant is not incorporated to remove sulfur dioxide, it was decided to test downstream of the primary precipitators where prior tests had indicated mercury concentrations in the presence of high levels of sulfur dioxide. The duct diameter at that point (see Figure 4-5) was four feet and was located approximately two pipe diameters upstream of a bend in the pipe. The nearest upstream disturbance was approximately twenty pipe diameters.

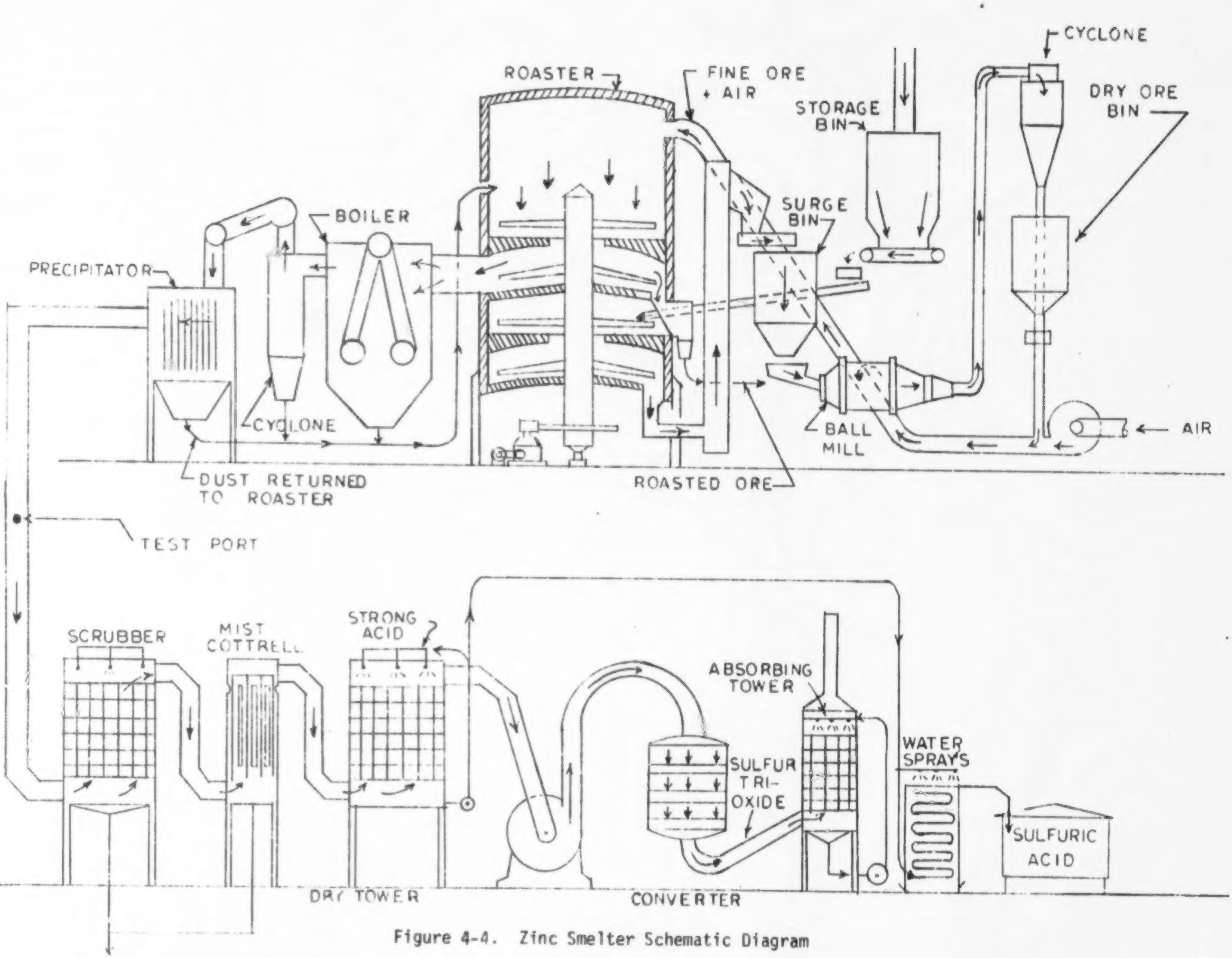

ROASTER
FINE ORE + AIR
CYCLONE
STORAGE BIN
DRY ORE BIN
SURGE BIN
BOILER
PRECIPITATOR
CYCLONE
BALL MILL
AIR
DUST RETURNED TO ROASTER
ROASTED ORE
TEST PORT
SCRUBBER
MIST COTTRELL
STRONG ACID
ABSORBING TOWER
WATER SPRAYS
SULFUR TRI-OXIDE
SULFURIC ACID
DRY TOWER
CONVERTER

Figure 4-4. Zinc Smelter Schematic Diagram

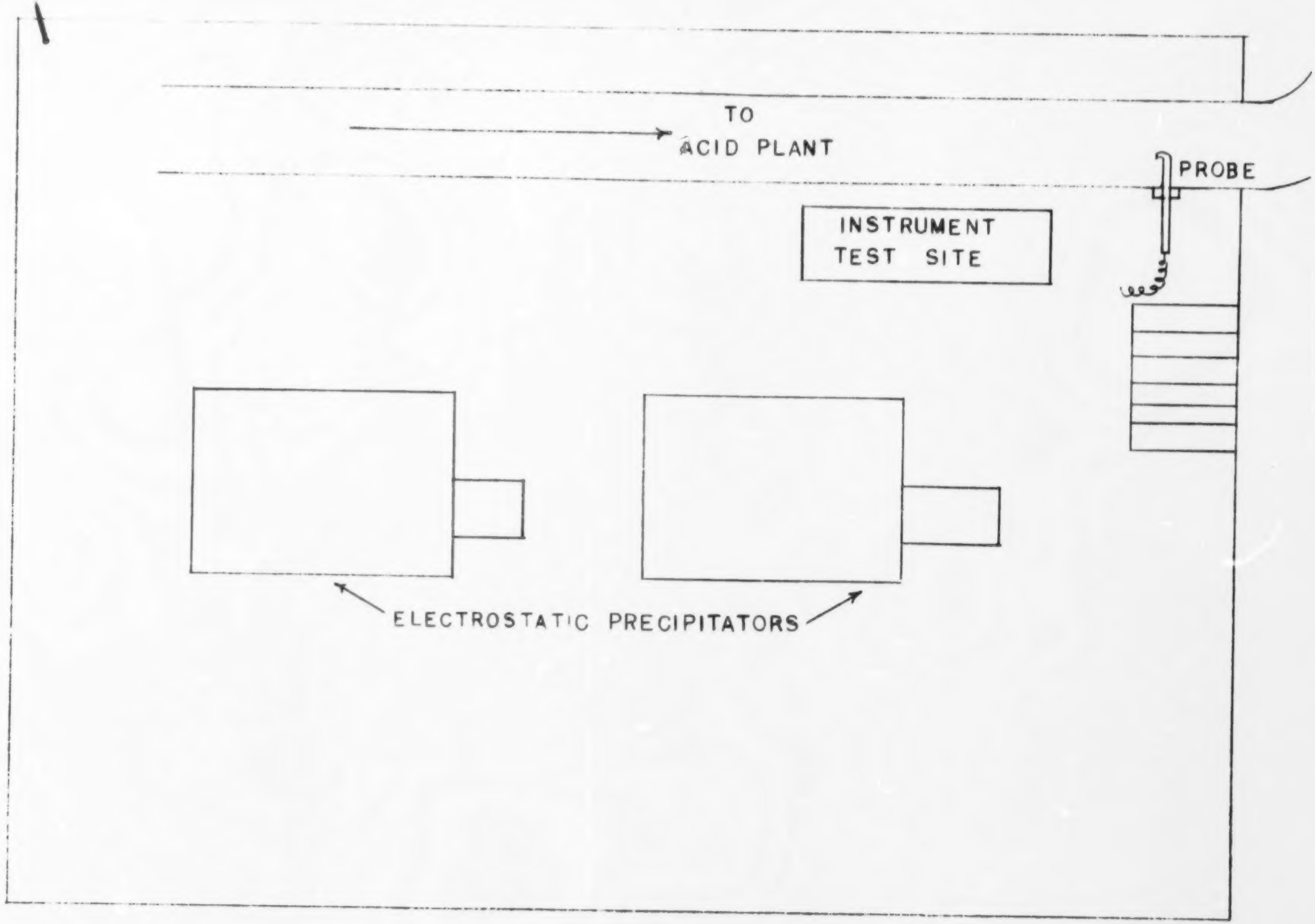

TO
ACID PLANT
PROBE
INSTRUMENT
TEST SITE
ELECTROSTATIC PRECIPITATORS

Figure 4-5. Schematic of Test Site at Zinc Smelter

2. Test Results

Due to excessively high ambient levels of sulfur dioxide in the test area, continuous instrument readings were usually not obtainable as the test personnel were forced to evacuate the test area. Gas leakage in the duct upstream of the primary precipitator and through the precipitator doors due to problems associated with the acid plant fan bearings was the source of the unusually high ambient levels of sulfur dioxide. A schematic of the test area is shown in Figure 4-5. Throughout the test period, the plant was shut down to repair the fan, but attempts were unsuccessful.

The Dupont unit had been fitted with a two-inch cell and associated filters used to correct for the interference of sulfur dioxide. The Dupont unit, with the short cell, had been preliminarily calibrated by a Dupont representative at the Walden laboratory. The Geomet unit could not be zeroed or achieve a steady background level of mercury, therefore, no data was obtained on the Geomet monitor, at this site. A sodium carbonate scrubber was placed upstream of the Beckman and Sunshine units. The pyrolyzer temperature was adjusted to 600°C, while the duct temperature averaged 500°F. The data obtained at this site is shown in Table 4-7.

On June 22, intermittent readings were taken that indicated the Dupont instrument to be recording substantially higher levels of mercury than the Beckman and Sunshine. However, further tests were cut short as the plant shut down. It was discovered that the Teflon nozzle and that part of the sampling line exposed to the high gas temperatures decomposed. Consequently, the original sampling system containing the sampling tee off of the glass lined probe was employed.

The following day, the system was operable for a short period at which time the sodium carbonate scrubber was relocated so that the gas stream entering the Dupont instrument was also scrubbed. Prior to this change, instrument readings were taken. Following the relocation of the scrubber, the Beckman and Sunshine units continued to indicate almost no change in concentration, while the Dupont unit dropped from 1.90 to 0.75 milligrams per cubic meter. Apparently, the Dupont unit had not been completely cancelling sulfur dioxide as an interferrent.

TABLE 4-7

TEST RESULTS AT ZINC SMELTER

Date-Time	Dilution Ratio	Milligrams per Cubic Meter		
		Beckman	Dupont	Sunshine
6/22/73				
10:05	--	>1	3.60	>1
10:20	2.49	0.58	2.45	0.50
10:55	2.78	0.47	1.20	0.35
11:00	2.78	>1	2.30	>1
11:40	2.82	>1	>4.0	>1
6/23/73				
9:15	--	0.95	2.2	>1
9:45	2.24	0.48	1.85	0.59
10:00	2.24	0.40	1.90	0.58
10:35	2.24	0.37	0.75	0.56
10:40	2.73	0.46	0.72	0.58
10:45	2.45	0.56	0.78	0.62

No useful data could be obtained the following three days due to the excessive sulfur dioxide levels and plant shut downs. It was decided to cancel the remaining test schedule due to the dangerous testing conditions.

It was qualitatively determined that the Dupont filtering system did not completely remove the interference of sulfur dioxide. Also, it was shown that sodium carbonate did scrub out sulfur dioxide, yet it was not proven whether 100 percent removal was achieved. However, the laboratory study successfully demonstrated this point.

V. CONCLUSIONS

The Olin instrument, when applied with a proper sample interface system, can perform adequately for use as a continuous stationary source monitor. It was particularly adaptable to applications at chlor-alkali plants because of the stannous chloride scrubber incorporated in its sampling system. The precision and accuracy of the unit in the laboratory program was exceptionally good with a range of 0-2.0 milligrams per cubic meter. However, the Olin monitor must be used, as would the other instruments, in conjunction with a highly accurate dynamic dilution system. The Dupont unit did not perform well in the laboratory or field, yet the instrument should be adequate as a continuous monitor if properly adjusted. The problems associated with this instrument were strictly due to calibration errors and improper cell path length. The potential ability of the instrument was verified by the test results of the Olin unit, which contains the complete Dupont analyzer. The Olin unit was independently calibrated and contained a shorter cell than the Dupont unit.

The Beckman monitor performed extremely well in the laboratory and field, although the unit is not designed for continuous use. As a lightweight, sturdy instrument, the Beckman could be employed as a portable continuous monitor if a portable sample interface subsystem could be designed. The Sunshine unit did not perform well in the laboratory or field and was not found acceptable for determining mercury emissions from stationary sources.

The data obtained from the Geomet instrument was limited and inconclusive. The high sensitivity of the unit posed considerable problems, yet there were some indications that the instrument might have application as a continuous monitor. It was found that the RAC Tape Stain Sampler would require major modifications beyond the scope of this study to adapt the instrument to a continuous monitoring mode. Therefore, it was decided early in the laboratory phase that a tape stain sampler would not be evaluated any further.

The precision and accuracy of the monitoring instruments is greatly affected by the sampling interface system and its ability to transport a representative sample. The mercury concentrations sampled in the field ranged as high as forty milligrams per cubic meter setting the requirement for a dilution system capable of controlling the mercury concentration in the range of the instruments (normally 0-1.0 milligram per cubic meter). The system employed in the field performed less than adequately in terms of these requirements; however, sample treatment for interfering species and conversion of particulate and organomercury compounds to elemental mercury was accomplished successfully. The laboratory results indicated that sodium carbonate absorbed sulfur dioxide without removal of mercury and all species of mercury tested were converted to elemental mercury by pyrolysis in the Geomet catalytic converter.

The hydrogen stream test results indicated that mercury species other than elemental mercury were present. Therefore, total mercury monitoring of chlor-alkali hydrogen lines would require some means of gas stream pyrolysis to convert particulate mercury or organomercury species to elemental form.

VI. RECOMMENDATIONS

There are presently no instruments available that can easily be employed as continuous stationary source monitors. Certain instruments, such as the Olin and Dupont units, can be adapted to continuous monitoring with the addition of sampling interface equipment that dilute the mercury source concentrations to those levels provided in the instruments. There are definite areas where further study and development are recommended, such as:

(1) Development studies should be performed on the dual beam instruments to determine if they can be modified to monitor mercury concentrations encountered at stationary sources without the use of a dynamic dilution system.

(2) Further study of sample interface subsystems should be made to develop possible schemes for automatic dynamic dilution systems.

(3) Although the field and laboratory results provided data to characterize the applicability and accuracy of the several types of instruments, additional data would be very useful and further work is recommended.

(4) Additional development of the Geomet dilution kit should be made to obtain an operating scheme applicable to stationary source monitoring. Additional study of this instrument should be made to obtain more complete data and to evaluate the operating parameters in a laboratory program.

(5) Further field studies should be made to determine the reliability of the Beckman unit as a portable monitor.

(6) Other dual-beam instruments should be studied to determine their performance as continuous monitors in comparison to

the Olin and Dupont instrument results. The study should provide sufficient data to determine the applicability of dual-beam instruments, as a class, for use as continuous monitors.

(7) Investigation of a pyrolyzer that can safely be used in the presence of hydrogen should be made so that future instrument studies on chlor-alkali hydrogen streams can be evaluated in terms of total mercury monitoring.

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APPENDIX A

TABLE 3-5

LABORATORY DATA FOR BECKMAN

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Beckman Reading mg/m^3
12/18/72	142	3693	4.9	27.0	0.18	0.20
	350	2536	5.25	8.25	0.64	0.72
	452	2444	3.5	6.41	0.55	0.68
	470	2444	3.5	6.20	0.56	0.64
	288	2462	4.3	9.55	0.45	0.30
	327	3997	4.2	13.22	0.32	0.28
	485	1756	3.6	4.62	0.78	0.77
	470	3694	4.0	8.86	0.45	0.45
	440	1827	4.4	5.15	0.85	0.85
1/9/73	270	2654	4.3	10.83	0.40	0.40
1/12/73	300	3299	4.4	12.00	0.37	0.34
	407	2319	4.1	6.70	0.61	0.64
	507	2321	3.9	5.58	0.70	0.82
	355	2526	3.9	8.12	0.48	0.35
	568	2455	3.5	5.32	0.66	0.75
	358	3467	4.4	10.68	0.41	0.33
	525	2575	3.8	5.90	0.64	0.64
	540	1825	3.8	4.38	0.87	0.95
	550	1825	3.8	4.32	0.88	0.89
1/19/73	200	3355	4.8	17.78	0.27	0.28
	405	3730	4.4	10.21	0.43	0.35
	540	3430	4.15	7.35	0.56	0.60
	573	3280	4.0	6.72	0.59	0.65
	615	3000	3.9	5.88	0.66	0.70
2/12/73	485	2360	2.6	5.87	0.44	0.40
2/27/73	200	1950	2.2	10.75	0.20	0.13
	350	1850	2.2	6.29	0.35	0.24
3/5/73	125	2200	2.2	18.60	0.12	0.11

TABLE 3-5 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Beckman Reading mg/m^3
3/5/73	65	2200	2.2	34.85	0.063	0.06
	125	2200	2.2	18.60	0.12	0.12
	165	2200	2.2	14.33	0.15	0.13
	205	2200	2.2	11.73	0.19	0.18
	310	2200	2.2	8.10	0.27	0.30
	380	2200	2.2	6.79	0.32	0.38
3/7/73	460	1350	2.3	3.93	0.58	0.60
	450	1350	2.3	4.00	0.57	0.51
	630	1350	2.3	3.14	0.73	0.78
	710	1350	2.35	2.90	0.81	0.85
	105	3175	2.4	31.24	0.077	0.076
	235	2135	2.5	10.09	0.25	0.18
	315	1900	2.45	7.03	0.35	0.29
	497	1580	2.4	4.18	0.57	0.54
	637	1380	2.4	3.17	0.76	0.75
	672	1350	2.4	3.01	0.80	0.81
3/19/73	190	2830	2.2	15.89	0.14	0.13
	272	2150	2.2	8.90	0.25	0.19
	457	2150	2.2	5.70	0.39	0.36
	446	1650	2.2	4.70	0.47	0.42
	533	1475	2.2	3.77	0.58	0.55
	672	1380	2.2	3.05	0.72	0.67
	680	1090	2.2	2.60	0.85	0.79
3/20/73	135	3350	2.2	25.81	0.085	0.075
	225	2870	2.2	13.76	0.16	0.16
	300	2550	2.3	9.50	0.24	0.21
	396	2280	2.25	6.76	0.33	0.30
	456	1950	2.25	5.28	0.43	0.45
	540	1620	2.25	4.00	0.56	0.60
	655	1380	2.25	3.11	0.72	0.83
	700	1200	2.25	2.71	0.83	0.91
	720	1000	2.2	2.39	0.92	1.00

TABLE 3-5 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Beckman Reading mg/m^3
3/21/73	180	2250	2.2	13.50	0.16	0.18
	265	1970	2.2	8.43	0.26	0.32
	135	2140	2.2	16.85	0.13	0.13
	207	2140	2.25	11.34	0.20	0.22
	328	2075	2.25	7.33	0.31	0.30
	397	1650	2.25	5.16	0.44	0.45
	488	1650	2.25	4.38	0.51	0.53
	533	1420	2.25	3.66	0.61	0.62
	653	1420	2.25	3.17	0.71	0.75
	722	1280	2.25	2.77	0.81	0.83
3/22/73	125	2600	2.2	21.80	0.10	0.11
	167	2225	2.25	14.32	0.16	0.18
	363	2200	2.25	7.06	0.32	0.35
	446	1970	2.25	5.42	0.42	0.46
	525	1550	2.25	3.95	0.57	0.62
	688	1545	2.25	3.25	0.69	0.83
	727	1280	2.25	2.76	0.82	0.92
	605	1150	2.3	2.90	0.79	0.87
	605	1600	2.35	3.64	0.64	0.78
	488	1625	2.35	4.33	0.54	0.61
	415	1730	2.45	5.17	0.47	0.50
	300	1750	2.5	6.83	0.37	0.36
	197	1970	2.6	11.00	0.24	0.22
	222	3017	2.6	14.59	0.18	0.16
	180	3300	2.7	19.33	0.14	0.13

$$^{*}\text{Dilution ratio} = \frac{\text{Dilution flow + Hg flow}}{\text{Hg flow}}$$

TABLE 3-6

LABORATORY DATA FOR OLIN

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Olin Reading mg/m^3
3/8/73	195	1750	2.3	9.97	0.23	0.22
	320	1720	2.3	6.38	0.35	0.36
	415	1720	2.3	5.14	0.45	0.45
	410	1600	2.35	4.90	0.48	0.51
	178	3080	2.35	18.30	0.13	0.14
	365	3030	2.35	9.30	0.25	0.22
	361	2330	2.3	7.45	0.31	0.30
	361	1925	2.4	6.33	0.38	0.38
	458	1850	2.4	5.04	0.48	0.48
	460	1580	2.4	4.43	0.54	0.56
	537	1430	2.4	3.66	0.66	0.68
	652	1280	2.4	2.96	0.81	0.87
3/9/73	167	3070	2.25	19.38	0.12	0.08
	228	2720	2.25	12.93	0.17	0.19
	300	2450	2.3	9.17	0.25	0.26
	388	2200	2.3	6.67	0.34	0.38
	420	1850	2.35	5.40	0.43	0.48
	430	1500	2.2	4.49	0.49	0.52
	472	1470	2.25	4.11	0.55	0.61
	563	1550	2.25	3.76	0.60	0.64
3/12/73	83	3035	2.2	37.57	0.059	0.05
	213	3025	2.25	15.20	0.15	0.13
	292	2810	2.25	10.62	0.21	0.19
	368	2310	2.25	7.28	0.31	0.29
	430	1925	2.25	5.48	0.41	0.40
	427	1400	2.25	4.28	0.53	0.49
	515	1350	2.25	3.62	0.62	0.58
	575	1350	2.25	3.35	0.67	0.65
	638	1270	2.25	2.99	0.75	0.74
	693	1050	2.25	2.52	0.89	0.91

TABLE 3-6 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Olin Reading mg/m^3
3/12/73	667	870	2.25	2.30	0.98	0.97
	670	1150	2.25	2.72	0.83	0.85
3/13/73	555	1100	2.2	2.98	0.74	0.71
	605	1100	2.2	2.82	0.78	0.78
	653	1100	2.2	2.68	0.82	0.82
	705	1030	2.2	2.46	0.89	0.92
	705	920	2.2	2.31	0.95	0.97
	670	1050	2.35	2.57	0.92	0.92
	670	920	2.4	2.37	1.01	0.99

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*Dilution ratio = $\frac{\text{Dilution flow + Hg flow}}{\text{Hg flow}}$

TABLE 3-7

LABORATORY DATA FOR SUNSHINE

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Sunshine Reading mg/m^3
1/19/73	200	3355	4.8	17.78	0.27	0.25
	405	3730	4.4	10.21	0.43	0.47
	540	3430	4.15	7.35	0.56	0.80
	573	3280	4.0	6.72	0.59	0.85
	615	3000	3.9	5.88	0.66	0.86
2/27/73	200	1950	2.2	10.75	0.20	0.18
	350	1850	2.2	6.29	0.35	0.25
3/5/73	125	2200	2.2	18.60	0.12	0.12
	65	2200	2.2	34.85	0.063	0.05
	125	2200	2.2	18.60	0.12	0.11
	165	2200	2.2	14.33	0.15	0.13
	205	2200	2.2	11.73	0.19	0.19
	310	2200	2.2	8.10	0.27	0.28
	380	2200	2.2	6.79	0.32	0.35
3/7/73	460	1350	2.3	3.93	0.58	0.65
	450	1350	2.3	4.00	0.57	0.47
	630	1350	2.3	3.14	0.73	0.71
	710	1350	2.35	2.90	0.81	0.67
	105	3175	2.4	31.24	0.077	0.14
	235	2135	2.5	10.09	0.25	0.27
	315	1900	2.45	7.03	0.35	0.36
	497	1580	2.4	4.18	0.57	0.59
	637	1380	2.4	3.17	0.76	0.72
	672	1350	2.4	3.01	0.80	0.74
3/8/73	195	1750	2.3	9.97	0.23	0.22
	320	1720	2.3	6.38	0.35	0.28
	415	1720	2.3	5.14	0.45	0.49
	410	1600	2.35	4.90	0.48	0.53
	178	3080	2.35	18.30	0.13	0.18
	365	3030	2.35	9.30	0.25	0.33

TABLE 3-7 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Sunshine Reading mg/m^3
3/8/73	361	2330	2.3	7.45	0.31	0.28
	361	1925	2.4	6.33	0.38	0.34
	458	1850	2.4	5.04	0.48	0.42
	460	1580	2.4	4.43	0.54	0.48
	537	1430	2.4	3.66	0.66	0.57
	652	1280	2.4	2.96	0.81	0.70
3/9/73	167	3070	2.25	19.38	0.12	0.18
	228	2720	2.25	12.93	0.17	0.26
	300	2450	2.3	9.17	0.25	0.34
	388	2200	2.3	6.67	0.34	0.44
	420	1850	2.35	5.40	0.43	0.43
	430	1500	2.2	4.49	0.49	0.57
	472	1470	2.25	4.11	0.55	0.48
	563	1500	2.25	3.76	0.60	0.62
3/14/73	225	1675	2.3	8.44	0.27	0.38
	460	1430	2.3	4.11	0.56	0.92
	590	1100	2.25	2.86	0.78	1.00
	150	880	2.2	6.87	0.32	0.40
	682	1080	2.4	2.58	0.93	0.85
3/15/73	210	1530	2.4	8.29	0.29	0.32
	390	1560	2.4	5.00	0.48	0.65
	333	1260	2.35	4.78	0.49	0.41
	455	1525	2.35	4.35	0.54	0.65
	600	2010	2.35	4.35	0.54	0.63
	660	2010	2.35	4.05	0.58	0.74
	333	3500	2.3	11.51	0.20	0.30
	258	2115	2.3	9.20	0.25	0.35
	298	2035	2.35	7.83	0.30	0.39
	250	2900	2.4	12.60	0.19	0.19
	375	1540	2.4	5.11	0.47	0.63
3/16/73	573	1900	2.2	4.32	0.51	0.64
	520	2200	2.2	5.23	0.42	0.74

TABLE 3-7 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Sunshine Reading mg/m^3
3/16/73	497	1605	2.2	4.23	0.52	0.58
	625	1745	2.2	3.79	0.58	0.58
	640	2240	2.25	4.50	0.50	0.64
	583	1680	2.25	3.88	0.58	0.59
	710	1825	2.25	3.57	0.63	0.74
	485	1940	2.3	5.00	0.46	0.58
	352	1670	2.3	5.74	0.40	0.65
3/23/73	230	1305	2.4	6.67	0.36	0.22
	295	1180	2.4	5.00	0.48	0.75
	420	1315	2.4	4.13	0.58	0.77
	490	2260	2.3	5.61	0.41	0.31

$$^{*}\text{Dilution ratio} = \frac{\text{Dilution flow + Hg flow}}{\text{Hg flow}}$$

TABLE 3-8

LABORATORY DATA FOR DUPONT TWENTY INCH CELL

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Dupont Reading mg/m^3
3/1/73	693	1200	2.2	2.73	0.81	0.53
	693	1600	2.22	3.31	0.67	0.47
	675	1650	2.24	3.44	0.65	0.46
	648	1730	2.27	3.67	0.62	0.44
	540	1620	2.32	4.00	0.58	0.41
	540	1950	2.32	4.61	0.50	0.385
	543	2810	2.35	6.18	0.38	0.30
	458	2810	2.37	7.14	0.33	0.27
	412	2820	2.5	7.84	0.32	0.25
	250	2820	2.5	12.28	0.20	0.18
	215	2840	2.32	14.21	0.16	0.15
	230	2840	2.3	13.35	0.17	0.16
	275	3370	2.42	13.25	0.18	0.16
3/19/73	190	2830	2.2	15.89	0.14	0.10
	272	2150	2.2	8.90	0.25	0.19
	457	2150	2.2	5.70	0.39	0.30
	446	1650	2.2	4.70	0.47	0.36
	533	1475	2.2	3.77	0.58	0.42
	672	1380	2.2	3.05	0.72	0.50
	680	1090	2.2	2.60	0.85	0.56
	712	1000	2.2	2.40	0.91	0.59
3/20/73	135	3350	2.2	25.81	0.085	0.06
	225	2870	2.2	13.76	0.16	0.14
	300	2550	2.3	9.50	0.24	0.20
	396	2280	2.25	6.76	0.33	0.28
	456	1950	2.25	5.28	0.43	0.36
	540	1620	2.25	4.00	0.56	0.45
	655	1380	2.25	3.11	0.72	0.54
	700	1200	2.25	2.71	0.83	0.585
	720	1000	2.2	2.39	0.92	0.62
	750	900	2.25	2.20	1.02	0.65

TABLE 3-8 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Dupont Reading mg/m^3
3/21/73	180	2250	2.2	13.50	0.16	0.15
	265	1970	2.2	8.43	0.26	0.24
	135	2140	2.2	16.85	0.13	0.09
	207	2140	2.25	11.34	0.20	0.17
	328	2075	2.25	7.33	0.31	0.27
	397	1650	2.25	5.16	0.44	0.38
	488	1650	2.25	4.38	0.51	0.435
	533	1420	2.25	3.66	0.61	0.485
	653	1420	2.25	3.17	0.71	0.55
	722	1280	2.25	2.77	0.81	0.59
3/22/73	125	2600	2.2	21.80	0.10	0.08
	167	2225	2.25	14.32	0.16	0.16
	363	2200	2.25	7.06	0.32	0.27
	446	1970	2.25	5.42	0.42	0.36
	525	1550	2.25	3.95	0.57	0.445
	688	1545	2.25	3.25	0.69	0.545
	727	1280	2.25	2.76	0.82	0.59
	727	1000	2.3	2.38	0.97	0.62
	605	1150	2.3	2.90	0.79	0.56
	605	1600	2.35	3.64	0.64	0.51
	488	1625	2.35	4.33	0.54	0.435
	415	1730	2.45	5.17	0.47	0.37
	300	1750	2.5	6.83	0.37	0.28
	197	1970	2.6	11.00	0.24	0.19
	222	3017	2.6	14.59	0.18	0.14
	180	3300	2.7	19.33	0.14	0.11

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*Dilution ratio = $\frac{\text{Dilution flow + Hg flow}}{\text{Hg flow}}$

TABLE 3-9

LABORATORY DATA FOR DUPONT TWO INCH CELL

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Dupont Reading mg/m^3
7/4/73	370	2020	2.25	6.46	0.35	0.48
	445	2020	2.25	5.54	0.41	0.60
	450	2275	2.3	6.06	0.38	0.56
	480	1850	2.2	4.85	0.45	0.61
	463	1450	2.2	4.13	0.53	0.73
	420	1125	2.3	3.68	0.62	0.74
	447	1125	2.3	3.52	0.65	0.84
7/5/73	107	2310	2.55	22.59	0.11	0.16
	130	2250	2.2	18.31	0.13	0.21
	230	2140	2.2	10.30	0.21	0.27
	290	1900	2.2	7.55	0.29	0.35
	400	1900	2.2	5.75	0.38	0.49
	407	1350	2.2	4.32	0.51	0.65
	415	1025	2.25	3.47	0.65	0.78
	478	1035	2.25	3.17	0.71	0.94
	458	1035	2.25	3.26	0.69	0.90
	458	950	2.30	3.07	0.75	0.96
	110	2280	2.2	21.73	0.10	0.09
7/6/73	152	2250	2.25	15.80	0.14	0.14
	173	2200	2.25	13.72	0.16	0.16
	238	2200	2.2	10.24	0.21	0.24
	238	1925	2.25	9.09	0.25	0.28
	253	1670	225	7.60	0.30	0.32
	257	1472	2.3	6.73	0.34	0.37
	250	1150	2.3	5.60	0.41	0.46
	300	1150	2.2	4.83	0.46	0.53
	340	1150	2.2	4.38	0.50	0.62
7/7/73	370	1075	2.2	3.91	0.56	0.71
	415	1055	2.25	3.54	0.64	0.83
	422	875	2.25	3.07	0.73	0.97

TABLE 3-9 (continued)

Date	Hg Flow cc/min	Dilution Flow cc/min	Hg Conc. at Exit of Condenser mg/m^3	Dilution Ratio*	Calculated Hg Conc. mg/m^3	Dupont Reading mg/m^3
7/7/73	80	2312	2.35	29.90	0.08	0.11
	293	1950	2.35	7.66	0.31	0.32
	372	2050	2.3	6.51	0.35	0.43
	400	1950	2.3	5.88	0.39	0.51
	397	1700	2.38	5.28	0.45	0.57
	412	1020	2.43	3.48	0.70	0.865
	400	1040	2.5	3.60	0.69	0.82

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*Dilution ratio = $\frac{\text{Dilution flow + Hg flow}}{\text{Hg flow}}$

TABLE 4-1

RED OXIDE OF MERCURY TEST RESULTS

Date-Time	Instrument Readings Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3	Dilution Ratio	Stream Concentration* Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3
4/17/73							
10:30	.17	.16	.15	No dilution air			
10:45	.25	.24	.18	No dilution air			
10:50	.33	.31	.21	No dilution air			
10:55	.60	.66	.16	No dilution air			
11:15	.45	.40	.13	No dilution air			
11:30	.52	.58	.15	No dilution air			
11:45	.63	.71	.17	No dilution air			
12:00	.44	.41	.14	No dilution air			
1:15	.71	.83	.19	No dilution air			
1:25	.53	.49	.10	No dilution air			
1:40	.42	.37	.08	No dilution air			
1:55	.48	.45	.09	No dilution air			
4/18/73							
9:45		.30	.05	No dilution air			
9:55		.36	.05	No dilution air			
10:00		.42	.05	No dilution air			
10:05		.37	.04	No dilution air			
10:10		.33	.02	No dilution air			
10:15		.34	.02	No dilution air			

TABLE 4-1 (Continued)

	Instrument Readings				Stream Concentration*		
Date-Time	Beckman mg/m3	Sunshine mg/m3	Dupont mg/m3	Dilution Ratio	Beckman mg/m3	Sunshine mg/m3	Dupont mg/m3
10:20		.32	.02	No dilution air			
10:25		.38	.04	No dilution air			
10:30		.36	.03	No dilution air			
10:40		.40	.04	No dilution air			
10:50		.42	.04	No dilution air			
10:55		.40	.04	No dilution air			
11:00		.34	.04	No dilution air			
11:05		.38	.03	No dilution air			
11:10		.44	.03	No dilution air			
11:20		.30	.05	No dilution air			
11:25		.32	.05	No dilution air			
11:35		.38	.04	No dilution air			
4/19/73							
11:00	.15	.14	.04	No dilution air			
11:05	.15	.14	.04	No dilution air			
11:10	.15	.12	.045	No dilution air			
11:15	.17	.13	.048	No dilution air			
11:20	.19	.14	.053	No dilution air			
11:25	.17	.13	.05	No dilution air			
11:30	.14	.10	.044	No dilution air			
11:35	.16	.13	.043	No dilution air			
11:40	.16	.13	.043	No dilution air			

TABLE 4-1 (Continued)

	Instrument Readings				Stream Concentration*		
Date-Time	Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3	Dilution Ratio	Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3
11:45	.15	.14	.044	No dilution air			
11:50	.16	.15	.046	No dilution air			
11:55	.15	.14	.047	No dilution air			
12:00	.11	.08	.035	No dilution air			
4/20/73							
2:00	.12	.09	.04	No dilution air			
2:05	.13	.08	.04	No dilution air			
2:10	.15	.10	.05	No dilution air			
2:15	.13	.09	.04	No dilution air			
2:20	.11	.08	.04	No dilution air			
2:25	.13	.09	.042	No dilution air			
2:30	.13	.09	.043	No dilution air			
2:35	.13	.10	.044	No dilution air			
2:40	.14	.12	.048	No dilution air			
2:45	.14	.12	.046	No dilution air			
2:50	.15	.13	.047	No dilution air			
2:55	.16	.14	.05	No dilution air			
3:00	.16	.14	.049	No dilution air			
3:05	.14	.13	.050	No dilution air			
3:10	.15	.14	.053	No dilution air			
3:15	.16	.14	.053	No dilution air			
3:20	.17	.15	.057	No dilution air			

TABLE 4-1 (Continued)

Date-Time	Instrument Readings Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3	Dilution Ratio	Stream Concentration* Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3
3:25	.20	.17	.065	No dilution air			
3:30	.18	.16	.060	No dilution air			
3:35	.19	.17	.060	No dilution air			
3:40	.19	.16	.058	No dilution air			
3:45	.21	.17	.063	No dilution air			
3:50	.18	.15	.055	No dilution air			
3:55	.18	.15	.057	No dilution air			
4:00	.19	.16	.058	No dilution air			
4:05	.18	.16	.055	No dilution air			
4:10	.20	.17	.060	No dilution air			
4:15	.20	.18	.058	No dilution air			
4:20	.16	.16	.053	No dilution air			
4:25	.17	.18	.054	No dilution air			
4:30	.19	.19	.057	No dilution air			
4:35	.22	.21	.062	No dilution air			
4:40	.25	.26	.068	No dilution air			
4:45	.26	.27	.066	No dilution air			
4/23/73							
8:40	.12	.14	.043	No dilution air			
8:45	.12	.13	.044	No dilution air			
8:50	.13	.14	.047	No dilution air			
8:55	.12	.13	.043	No dilution air			

TABLE 4-1 (Continued)

Date-Time	Instrument Readings Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3	Dilution Ratio	Stream Concentration* Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3
9:00	.12	.13	.062	No dilution air			
9:05	.11	.13	.06	No dilution air			
9:10	.18	.21	.08	No dilution air			
9:15	.20	.22	.10	No dilution air			
9:20	.22	.20	.09	No dilution air			
9:25	.25	.23	.11	No dilution air			
9:30	.17	.14	.09	No dilution air			
9:35	.21	.18	.10	No dilution air			
10:55	.72	.63	.19	6.0	4.23	3.78	1.14
11:00	.85	.71	.23	7.2	6.12	5.11	1.66
11:05	.40	.10	.16	6.5	2.60	.65	1.04
11:10	.40	.05	.20	5.75	2.30	.29	.92
11:15	.36	0	.19	7.0	2.52	0	1.33
11:20	.40	---	.21	4.33	1.73	0	.91
11:25	.37	---	.20	3.25	1.20	0	.65
11:30	.48	---	.30	3.33	1.60	0	1.00
11:35	.74	.04	.31	2.75	2.04	.11	.85
11:40	.95	.13	.33	2.75	2.61	.36	.91
11:45	.90	.16	.31	2.75	2.48	.44	.85
11:50	.80	.10	.29	2.75	2.20	.28	.80
11:55	.70	.10	.30	2.75	1.93	.28	.83
12:00	.77	.12	.30	2.75	2.12	.33	.83
12:05	.83	.20	.30	2.75	2.28	.55	.83
12:10	.80	.22	.29	2.82	2.26	.62	.82
12:15	.79	.21	.28	2.82	2.23	.59	.79
12:20	.68	.16	.26	2.82	1.92	.45	.73

TABLE 4-1 (Continued)

	Instrument Readings				Stream Concentration*		
Date-Time	Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3	Dilution Ratio	Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3
12:25	.42	.16	.26	2.86	1.20	.46	.74
12:30	.15	.04	.21	2.98	.45	.12	.63
12:35	.10	.04	.21	3.12	.31	.12	.66
12:40	.02	.07	.16	3.28	.07	.23	.52
4/24/73							
9:20	>1.0	.55	.45	6.00	>6.00	3.3	2.7
9:30	.90	.72	.32	1.50	1.35	1.08	.48
9:35	.90	.60	.30	1.50	1.35	.9	.45
9:40	.85	.51	.17	1.50	1.28	.77	.26
9:45	.78	.43	.19	1.50	1.17	.65	.29
9:50	.72	.35	.16	1.50	1.08	.53	.24
10:00	.65	.30	.22	1.50	.98	.45	.33
10:05	.70	.38	.22	1.50	1.05	.57	.33
10:10	.72	.45	.27	1.50	1.08	.68	.41
10:15	.68	.43	.32	1.50	1.02	.65	.48
10:20	.68	.46	.25	1.50	1.02	.69	.38
10:25	.74	.57	.39	1.50	1.11	.86	.59
10:30	.86	.57	.40	1.20	1.03	.68	.48
10:35	.92	.59	.48	1.20	1.10	.71	.58
10:40	.84	.62	.49	No dilution air			
10:45	.83	.60	.52	No dilution air			
10:50	.87	.63	.55	No dilution air			
10:55	.89	.64	.58	No dilution air			
11:00	.90	.70	.57	No dilution air			
11:05	.90	.68	.54	No dilution air			
11:10	.96	.74	.58	No dilution air			
11:15	.88	.72	.56	No dilution air			

TABLE 4-1 (Continued)

	Instrument Readings				Stream Concentration*		
Date-Time	Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3	Dilution Ratio	Beckman mg/m^3	Sunshine mg/m^3	Dupont mg/m^3
11:20	.87	.71	.52	No dilution air			
11:25	.88	.71	.51	No dilution air			
11:30	.85	.68	.49	No dilution air			
11:35	.89	.68	.49	No dilution air			
11:40	.90	.70	.52	No dilution air			
11:45	.90	.72	.53	No dilution air			
11:50	.90	.73	.52	No dilution air			
12:00	.88	.70	.48	No dilution air			
1:20	.86	.71	.45	No dilution air			
1:30	.83	.70	.42	No dilution air			
1:35	.81	.68	.40	No dilution air			
1:45	.78	.65	.38	No dilution air			
1:55	.77	.61	.35	No dilution air			
2:00	.77	.60	.37	No dilution air			
2:10	.75	.60	.36	No dilution air			

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*Instrument readings multiplied by dilution ratio.

TABLE 4-3

CHLOR-ALKALI END-BOX STACK TEST RESULTS

Date Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration*				
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin	Geomet
5/17/73										
11:05	1.0	0.78	0.28		4.88	4.88	3.81	1.37		
11:25	0.67	0.52	0.24		4.74	3.18	2.46	1.14		
11:30	0.69	0.54	0.24		4.74	3.27	2.56	1.14		
11:35	0.66	0.51	0.22		4.74	3.13	2.42	1.04		
11:40	0.67	0.49	0.21		4.74	3.18	2.32	1.00		
11:45	0.66	0.49	0.21		4.74	3.13	2.32	1.00		
11:50	0.70	0.51	0.22		4.74	3.32	2.42	1.04		
12:55	0.87	0.77	0.34		4.85	4.22	3.73	1.65		
1:00	1.0	0.89	0.38		4.51	4.51	4.01	1.71		
1:05	1.0	0.85	0.39		5.18	5.18	4.40	2.02		
1:10	1.0	0.79	0.38		6.38	6.38	5.04	2.42		
1:15	>1.0	0.79	0.35		6.54	>6.54	5.17	2.92		
1:20	1.0	0.79	0.34		9.25	9.25	7.31	3.15		
1:25	1.0	0.80	0.38		7.14	7.14	5.71	2.71		
1:30	1.05	0.71	0.33		7.95	8.35	5.64	2.62		
1:35	0.99	0.61	0.29		9.75	9.65	5.95	2.83		
4:30	0.82	0.40	0.11	0.88	8.57	7.03	3.43	0.94	7.54	4.8
4:35	0.83	0.39	0.10	0.90	10.07	8.36	3.93	1.01	9.06	5.0
4:40	0.85	0.36	0.09	0.88	9.13	7.76	3.29	0.82	8.03	6.6
5/18/73										
10:20	0.91	0.24	0.055	0.88	6.88	6.26	1.65	0.38	6.05	
10:25	0.90	0.24	0.05	0.88	6.61	5.95	1.59	0.33	5.82	
10:30	0.95	0.23	0.053	0.91	6.61	6.28	1.52	0.35	6.02	
10:35	1.0	0.16	0.045	0.92	7.36	7.36	1.18	0.33	6.77	9.15
10:45	0.80	0.03	0.040	0.72	8.19	6.55	0.25	0.33	5.90	9.49
10:50	0.83	0.09	0.037	0.74	9.49	7.88	0.85	0.35	7.02	9.68
10:55	0.84	0.05	0.035	0.72	8.34	7.01	0.42	0.29	6.00	9.68
11:00	0.88	0.14	0.045	0.96	7.03	6.19	0.98	0.32	6.74	9.68
11:10	0.96	0.24	0.05	1.04	7.69	7.38	1.85	0.38	8.00	13.8
11:15	0.95	0.19	0.037	1.06	7.32	6.95	1.39	0.27	7.76	11.7

TABLE 4-3 (continued)

Date Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration*				
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin	Geomet
5/18/73										
11:20	1.0	0.19	0.04	1.06	8.44	8.44	1.60	0.34	8.95	11.4
11:25	1.0	0.22	0.041	1.04	8.44	8.44	1.86	0.35	8.78	11.45
11:35	1.05	0.26	0.075	1.16	8.69	9.12	2.26	0.65	10.08	>
11:45	0.95	0.18	0.067	1.06	15.53	14.75	2.80	1.04	16.46	>
12:00	0.90	0.16	0.062	1.12	18.22	16.40	2.92	1.13	20.41	16.5
5/21/73										
10:30	>1.0	0.31	0.09	1.5	6.92	>6.92	2.15	0.62	10.38	
10:40	>1.0	0.09	0.04	0.72	5.97	>5.97	0.54	0.24	4.30	
11:15	1.0	0.27	0.13	1.04	13.30	13.30	3.59	1.73	13.83	
11:20	0.95	0.20	0.12	0.96	13.64	12.96	2.73	1.64	13.09	
11:30	>1.0	0.29	0.19	1.02	57.88	>57.88	16.79	11.00	59.04	
11:35	>1.0	0.24	0.18	1.00	42.36	>42.36	10.17	7.62	42.36	
11:40	>1.0	0.22	0.19	0.98	22.67	>22.67	4.99	4.31	22.22	
2:00	0.67	0.14	0.14	0.60	6.43	4.31	0.90	0.90	3.86	
2:10	0.84	0.18	0.185	0.78	6.40	5.38	1.15	1.18	4.99	
2:15	0.92	0.08	0.19	0.82	6.52	6.00	0.52	1.24	5.35	
2:20	0.96	0.06	0.20	0.88	6.37	6.12	0.38	1.27	5.61	2.63
2:25	0.99	0	0.18	0.96	6.37	6.31	0	1.15	6.12	4.94
2:30	0.95	0.01	0.21	1.00	7.91	7.51	0.08	1.66	7.91	5.40
2:40	0.95	<0	0.21	1.08	8.31	7.89	<0	1.75	8.97	5.40
2:50	0.79	<0	0.20	0.96	10.32	8.15	<0	2.06	9.91	4.36
2:55	0.86	<0	0.19	1.11	10.32	8.88		1.96	11.45	
3:00	0.80	<0	0.16	1.06	10.32	8.26	<0	1.65	10.94	3.85
3:05	0.85	<0	0.17	1.10	10.32	8.77	<0	1.75	11.35	3.96
3:10	0.88	<0	0.19	1.15	10.06	8.85	<0	1.91	11.57	3.55
3:15	0.89	<0	0.19	1.23	10.06	8.95	<0	1.91	12.37	3.70
3:20	0.83	<0	0.17	1.20	10.32	8.57	<0	1.75	12.38	3.01
3:35	0.92		0.18	1.24	10.13	9.31		1.82	12.56	3.25
3:45	0.98		0.17	1.69	10.13	9.93		1.72	17.12	4.88
3:50	0.99		0.19	1.74	10.13	10.03		1.92	17.63	5.16
3:55	1.0		0.20	1.76	10.13	10.13		2.03	17.83	5.23
4:00	0.95		0.14	1.40	10.13	9.62		1.42	14.18	3.08

TABLE 4-3 (continued)

Date Time	Instrument Readings (mg/m^3) Beckman	Sunshine	Dupont	Olin	Dilution Ratio	Stream Concentration* Beckman	Sunshine	Dupont	Olin	Geomet
5/21/73										
4:10	0.98		0.16	1.56	10.26	9.93		1.62	15.80	4.21
4:15	0.97		0.15	1.46	10.13	9.83		1.52	14.79	4.08
4:25	0.95		0.14	1.44	10.20	9.62		1.42	14.59	4.49
4:35	0.94		0.21	1.46	10.13	9.52		2.13	14.79	3.58
4:40	0.93		0.19	1.48	10.13	9.42		1.92	14.99	3.27
5/22/73										
9:45	0.35		0.435	0.96	10.08	3.53		4.38	9.68	
9:50	0.35		0.425	0.98	10.84	3.81		4.63	10.67	
9:55	0.40		0.48	1.14	9.40	3.76		4.51	10.71	
10:00	0.44		0.50	1.24	9.15	4.03		4.58	11.35	
10:05	0.56		0.54	1.30	9.24	5.17		4.99	12.01	
10:10	0.70		0.55	1.36	9.30	6.51		5.12	12.65	14.37
10:15	0.62		0.525	1.36	9.62	5.96		5.05	13.08	16.38
10:20	0.55		0.51	1.26	9.15	5.03		4.67	11.53	12.96
10:25	0.55		0.50	1.12	9.62	5.29		4.81	10.77	11.47
10:30	0.48		0.475	1.20	9.90	4.75		4.70	11.88	10.12
10:45	0.85		0.17	1.08	9.98	8.48		1.70	10.78	7.35
10:50	0.88		0.16	1.30	9.90	8.71		1.58	12.87	7.07
11:35			0.49	0.96	6.43			3.15	6.43	
11:40			0.56	1.16	6.74			3.77	9.44	9.12
11:45			0.60	1.34	7.04			4.22	11.40	8.72
11:50			0.57	1.18	6.94			3.96	9.99	8.33
11:55			0.55	1.22	6.87			3.78	10.17	7.28
12:00			0.545	1.08	6.87			3.74	9.21	9.67
1:35			0.56		5.55			3.11		
1:40			0.555		5.61			3.11		
1:45			0.615	1.24	5.59			3.44	6.93	4.15
1:50			0.61	1.30	5.69			3.47	7.40	9.24
1:55			0.60	1.38	5.69			3.41	7.85	10.66
2:00			0.615	1.42	5.69			3.50	8.08	13.16
2:05			0.63	1.48	5.76			3.63	8.52	11.47
2:10			0.50	0.94	8.65			4.33	8.13	12.48
2:15			0.44	0.82	8.65			3.81	7.09	15.31

TABLE 4-3 (continued)

Date Time	Instrument Readings (mg/m^3) Beckman	 Sunshine	 Dupont	 Olin	Dilution Ratio	Stream Concentration* Beckman	 Sunshine	 Dupont	 Olin	 Geomet
5/22/73										
2:20			0.475	0.94	8.65			4.11	8.13	10.40
2:55			0.135	0.36	7.94			1.07	2.86	7.18
3:05			0.28	0.60	8.02			2.25	4.81	8.10
3:10			0.41	0.76	8.52			3.49	6.48	7.34
3:20			0.33	0.60	8.32			2.75	4.99	9.01
3:25			0.35	0.60	8.36			2.93	5.02	8.42
3:35			0.37	0.65	8.32			3.08	5.41	9.01
5/23/73										
11:05	0.97		0.63	1.24	7.62	7.39		4.80	9.45	
11:10	0.98		0.62	1.43	7.62	7.46		4.72	10.90	
11:15	1.00		0.64	1.52	9.53	9.53		6.10	14.49	
11:20	0.93		0.59	1.28	10.38	9.65		6.12	13.29	
11:25	0.85		0.555	1.22	11.95	10.15		6.63	14.58	
11:30	0.92		0.60	1.32	12.28	11.30		7.37	16.21	
11:35	0.80		0.55	1.04	16.32	13.06		8.98	16.97	
11:40	0.76		0.54	1.12	17.55	13.34		9.48	19.66	
1:00	0.60		0.45	0.68	6.11	3.67		2.75	4.15	
1:05	0.75		0.53	1.10	9.51	7.13		5.04	10.46	
1:10	0.58		0.45	0.78	15.55	9.02		7.00	12.13	
1:15	0.60		0.46	0.80	15.12	9.07		6.96	12.10	
1:25	0.67		0.49	1.00	17.00	11.39		8.33	17.00	
1:30	0.56		0.44	0.88	17.55	9.83		7.72	15.44	
1:35	0.75		0.51	1.22	17.96	13.47		9.16	21.91	
1:40	0.76		0.54	1.14	17.96	13.65		9.70	20.47	
1:45	0.78		0.52	1.14	18.96	14.79		9.86	21.61	
1:50	0.66		0.45	1.04	18.32	12.09		8.24	19.05	
1:55	0.54		0.425	0.86	17.72	9.57		7.53	15.24	
2:00	0.55		0.41	0.80	17.72	9.75		7.26	14.18	
2:05	0.77		0.51	1.12	17.72	13.64		9.04	19.85	
2:10	0.58		0.44	0.90	18.96	11.00		8.34	17.06	
3:35	0.58		0.40	0.65	19.70	11.43		7.88	12.81	
3:40	0.67		0.45	0.76	17.03	11.41		7.66	12.94	

TABLE 4-3 (continued)

Date Time	Instrument Readings (mg/m^3) Beckman	Sunshine	Dupont	Olin	Dilution Ratio	Stream Concentration* Beckman	Sunshine	Dupont	Olin	Geomet
5/23/73										
3:45	0.55		0.39	0.60	23.50	12.93		9.17	14.10	
3:50	0.60		0.42	0.66	21.83	13.10		9.17	14.41	
3:55	0.63		0.44	0.64	21.83	13.75		9.61	13.97	
4:00	0.64		0.43		21.83	13.97		9.39		
4:05	0.60		0.42	0.72	19.52	11.71		8.20	14.05	
4:10	0.60		0.415	0.72	21.83	13.10		9.06	15.72	
4:15	0.59		0.40	0.74	21.83	12.88		8.73	16.15	
4:20	0.58		0.41	0.76	21.83	12.66		8.95	16.59	
5/24/73										
10:25	0.67		0.51		12.05	8.07		6.15		
10:35	0.53		0.45		11.64	6.17		5.24		
10:50	0.35		0.34	0.54	6.54	2.29		2.22	3.53	
10:55	0.40		0.37		6.54	2.62		2.42		
11:00	0.46		0.415	0.66	6.54	3.01		2.71	4.32	
11:05	0.50		0.43	0.74	6.54	3.27		2.81	4.84	
11:10	0.54		0.44	0.76	6.54	3.53		2.88	4.97	
11:15	0.54		0.45	0.80	6.54	3.53		2.94	5.23	
11:20	0.37		0.36	0.56	6.73	2.49		2.42	3.77	
11:25	0.40		0.36	0.68	6.73	2.69		2.42	4.58	
11:30	0.58		0.46	0.85	6.83	3.96		3.14	5.81	
11:35	0.75		0.54	1.08	6.83	5.12		3.69	7.38	
11:40	0.55		0.45		6.73	3.70		3.03		
11:45	0.53		0.44	0.84	6.83	3.62		3.01	5.74	
11:50	0.53		0.43	0.84	6.83	3.62		2.94	5.74	
11:55	0.56		0.45	0.83	6.83	3.82		3.07	5.67	
12:00	0.76		0.53	1.11	6.83	5.19		3.62	7.58	
12:05	0.64		0.48	0.90	6.83	4.37		3.28	6.15	
12:10	0.58		0.47	0.92	6.83	3.96		3.21	6.28	
2:35	0.80		0.57	1.20	3.50	4.30		4.87	6.07	
2:40	0.86		0.60	1.40	3.88	3.33		2.33	5.43	
2:45	0.80		0.585	1.24	3.88	3.10		2.27	4.81	
2:50	0.93		0.60	1.40	3.88	3.61		2.33	5.43	
2:55	0.95		0.62	1.44	3.88	3.69		2.41	5.59	

TABLE 4-3 (continued)

Date Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration*				
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin	Geomet
5/24/73										
3:00	0.79		0.565	1.20	4.81	3.80		2.72	5.77	
3:05	0.68		0.51	1.02	4.88	3.32		2.49	4.98	
3:10	0.72		0.52	1.10	4.88	3.51		2.54	5.37	
3:20	0.80		0.55	1.08	4.88	3.90		2.68	5.27	
3:25	0.68		0.50	1.06	4.96	3.37		2.48	5.26	1.21
3:30	0.75		0.52	1.04	4.88	3.66		2.54	5.08	1.10
3:35	0.79		0.545	1.10	4.88	3.86		2.66	5.37	1.10
3:40	0.80		0.55	1.12	4.88	3.90		2.68	5.47	1.05
3:45	0.87		0.57	1.16	4.88	4.25		2.78	5.66	0.87
3:50	0.80		0.51	1.00	4.96	3.97		2.53	4.96	1.28
3:55	0.77		0.54	1.10	5.02	3.87		2.71	5.52	1.14
4:00	0.74		0.52	1.04	5.09	3.77		2.65	5.29	1.34
4:05	0.60		0.465	0.88	5.02	3.01		2.33	4.42	
4:10	0.68		0.49	0.96	5.02	3.41		2.46	4.82	
4:15	0.75		0.52	1.00	5.09	3.82		2.65	5.09	
4:20	0.65		0.48	0.89	5.02	3.26		2.41	4.47	
4:25	0.70		0.49	0.91	5.08	3.56		2.49	4.62	
5/25/73										
11:00	0.65		0.56	0.98	3.11	2.02		1.74	3.05	
11:05	0.60		0.52	0.92	3.17	1.90		1.65	2.92	
11:10	0.60		0.52	0.90	3.11	1.87		1.62	2.80	
11:15	0.83		0.59	1.16	3.13	2.60		1.85	3.63	
11:20	0.86		0.595	1.19	3.19	2.74		1.90	3.80	
11:25	0.85		0.605	1.20	3.23	2.75		1.95	3.88	
11:30	0.82		0.595	1.20	3.23	2.65		1.92	3.88	
11:35	0.64		0.53	0.94	3.29	2.11		1.74	3.09	
11:40	0.69		0.54	1.00	3.23	2.23		1.74	3.23	
11:45	0.79		0.585	1.13	3.17	2.50		1.85	3.58	
11:50	0.76		0.58	1.10	3.23	2.45		1.87	3.55	
11:55	0.67		0.54	1.00	3.23	2.16		1.74	3.23	
12:00	0.74		0.555	1.06	3.10	2.29		1.72	3.29	

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*Instrument readings multiplied by dilution ratio

TABLE 4-4

END-BOX SAMPLE TESTS

Date	Reference Tests (Stack Samples) Method	Instrument Stream Samples, Method	Hg Concentration by AA Analysis (mg/m^3)	Olin mg/m^3	Beckman mg/m^3	Dupont mg/m^3	Geomet mg/m^3
5/18		$KMnO_4$	1.28	1.05	0.97	0.048	1.50
5/21		$KMnO_4$	1.35	1.10	0.85	0.18	0.38
5/22		ICl	1.18	1.16		0.55	1.25
5/23		ICl	1.08	1.01	0.66	0.47	
5/23		$KMnO_4$	0.82	0.71	0.61	0.42	
5/24		$KMnO_4$	1.33	1.21	0.81	0.56	
5/21	ICl		35.01	15.15	9.63	1.75	4.02
5/24	ICl		35.30	5.44	3.58	2.93	
5/24	ICl		10.74	5.08	3.67	2.57	1.13
5/25	ICl		7.90	3.38	2.33	1.79	

TABLE 4-5

HYDROGEN STREAM TEST RESULTS

Date-Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration* (mg/m^3)			
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin
5/30/73									
2:50	0.64	0.74		0.66	23.94	15.32	17.72		15.80
2:55	0.61	0.68		0.64	23.94	14.60	16.28		15.32
3:05	0.57	0.59		0.63	23.94	13.65	14.12		15.08
3:10	0.56	0.56		0.62	23.94	13.41	13.41		14.84
3:15	0.55	0.54		0.62	23.94	13.17	12.93		14.84
3:25	0.54	0.49		0.62	23.94	12.93	11.73		14.84
3:35	0.53	0.45		0.62	23.94	12.69	10.77		14.84
3:45	0.50	0.40		0.61	23.94	11.97	9.58		14.60
3:55	0.50	0.36		0.62	23.94	11.97	8.62		14.84
4:00	0.49	0.33		0.62	23.94	11.73	7.90		14.84
4:05	0.51	0.30		0.64	23.94	12.21	7.18		15.32
4:10	0.54	0.28		0.65	23.66	12.78	6.62		15.38
4:15	0.55	0.26		0.66	23.94	13.17	6.22		15.80
4:25	0.57	0.24		0.68	23.94	13.65	5.75		16.28
4:35	0.55	0.23		0.66	23.94	13.17	5.51		15.80
4:40	0.52	0.25		0.64	23.94	12.45	5.99		15.32
4:45	0.53	0.22		0.63	23.66	12.54	5.21		14.91
4:50	0.51	0.20		0.63	23.66	12.07	4.73		14.91
5:00	0.52	0.17		0.62	23.66	12.30	4.02		14.67
5:10	0.54	0.19		0.63	23.66	12.78	4.50		14.91
5:15	0.56	0.16		0.67	23.94	13.41	3.83		16.04
5:20	0.56	0.18		0.65	23.94	13.41	4.31		15.56
5:30	0.53	0.18		0.63	23.94	12.69	4.31		15.08
5/31/73									
10:00	0.65	0.66		0.64	22.69	14.75	14.98		14.52
10:05	0.74	0.67		0.74	21.51	15.92	14.41		15.92
10:10	0.69	0.60		0.69	21.00	14.49	12.60		14.49
10:15	0.65	0.50		0.65	20.74	13.48	10.37		13.48
10:20	0.90	0.80		0.89	20.50	18.45	16.40		18.25
10:25	0.77	0.60		0.77	20.25	15.59	12.15		15.59

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3) Beckman	Instrument Readings (mg/m^3) Sunshine	Instrument Readings (mg/m^3) Dupont	Instrument Readings (mg/m^3) Olin	Dilution Ratio	Stream Concentration* (mg/m^3) Beckman	Stream Concentration* (mg/m^3) Sunshine	Stream Concentration* (mg/m^3) Dupont	Stream Concentration* (mg/m^3) Olin
10:30	0.77	0.51		0.79	19.57	15.07	9.98		15.46
10:35	0.83	0.54		0.86	18.22	15.12	9.84		15.67
10:40	0.53	0.36		0.56	23.14	12.26	8.33		12.96
10:45	0.81	0.52		0.81	17.85	14.46	9.28		14.46
10:50	0.74	0.44		0.76	19.45	14.39	8.56		14.78
10:55	0.75	0.44		0.80	15.81	11.86	6.96		12.65
11:00	0.80	0.49		0.79	15.81	12.65	7.75		12.49
11:10	0.67	0.46		0.72	17.00	11.39	7.82		12.24
11:20	0.78	0.49		0.81	18.39	14.34	9.01		14.90
11:25	0.90	0.52		0.92	17.00	15.30	8.84		15.64
11:30	0.75	0.46		0.78	19.18	14.39	8.82		14.96
11:35	0.82	0.48		0.84	19.18	15.73	9.21		16.11
11:40	0.73	0.44		0.77	21.00	15.33	9.24		16.17
11:45	0.78	0.46		0.80	18.39	14.34	8.46		14.71
11:50	0.72	0.40		0.75	19.18	13.81	7.67		14.39
2:10	0.69	0.50		0.81	21.00	14.49	10.50		17.01
2:40	0.70	0.43			22.88	16.02	9.84		
2:50	0.50	0.34		0.67	26.74	13.37	9.09		17.92
2:55	0.85	0.52		0.90	20.02	17.02	10.41		18.02
3:00	0.65	0.43		0.73	23.00	14.95	9.89		16.79
3:03	0.55	0.35		0.60	27.52	15.14	9.63		16.51
3:06	0.49	0.33		0.58	29.23	14.32	9.65		16.95
3:09	0.62	0.45		0.72	23.00	14.26	10.35		16.56
3:12	0.65	0.45		0.75	21.00	13.65	9.45		15.75
3:15	0.62	0.44		0.67	23.00	14.26	10.12		15.41
3:18	0.74	0.53		0.76	24.16	17.88	12.80		18.36
3:21	0.65	0.46		0.68	21.95	14.27	10.10		14.93
3:25	0.62	0.45		0.63	21.95	13.61	9.88		13.83
3:30	0.62	0.43		0.63	24.16	14.98	10.39		15.22

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3) Beckman	Sunshine	Dupont	Olin	Dilution Ratio	Stream Concentration* (mg/m^3) Beckman	Sunshine	Dupont	Olin
3:35	0.80	0.53		0.81	16.80	13.44	8.90		13.61
3:40	0.82	0.55		0.79	19.44	15.94	10.69		15.36
3:45	0.75	0.52		0.73	18.02	13.52	9.37		13.15
3:50	0.72	0.48		0.71	18.02	12.97	8.65		12.79
3:55	0.76	0.49		0.76	21.11	16.04	10.34		16.04
4:00	0.75	0.45		0.74	20.24	15.18	9.11		14.98
4:05	0.85	0.50		0.82	18.01	15.31	9.01		14.77
4:08	0.80	0.45		0.76	19.44	15.55	8.75		14.77
4:11	0.62	0.36		0.60	23.13	14.34	8.33		13.88
4:14	0.67	0.39		0.63	21.00	14.07	8.19		13.23
4:17	0.79	0.46		0.77	20.13	15.90	9.26		15.50
4:20	0.80	0.49		0.78	18.60	14.88	9.11		14.51
4:23	0.82	0.47		0.80	17.92	14.69	8.42		14.34
4:26	0.90	0.51		0.88	17.30	15.57	8.82		15.22
4:29	0.85	0.48		0.85	17.30	14.71	8.30		14.71
4:32	0.86	0.47		0.85	17.30	14.88	8.13		14.71
6/1/73									
10:35	0.97	0.67		0.94	17.39	16.87	11.65		16.35
10:40	0.76	0.56		0 75	23.13	17.58	12.95		17.35
10:45	0.80	0.54		0.73	22.07	17.66	11.92		16.11
10:48	0.77	0.56		0.75	22.07	16.99	12.36		16.55
10:51	0.76	0.58		0.73	22.07	16.77	12.80		16.11
10:54	0.74	0.57		0.67	24.29	17.97	13.85		16.27
10:57	0.80	0.61		0.73	21.11	16.89	12.88		15.41
11:00	0.64	0.52		0.60	24.92	15.95	12.96		14.95
11:03	0.77	0.59		0.72	21.95	16.90	12.95		15.80
11:06	0.90	0.66		0.84	20.13	18.12	13.29		16.91
11:09	0.87	0.63		0.80	20.13	17.51	12.68		16.10
11:12	0.76	0.58		0.71	20.13	15.30	11.68		14.29
11:15	0.83	0.64		0.79	20.13	16.71	12.88		15.90
11:16	0.70	0.55		0.72	21.00	14.70	11.55		15.12
11:19	0.73	0.56		0.76	21.92	16.00	12.28		16.66
11:22	0.80	0.60		0.83	21.00	16.80	12.60		17.43
11:25	0.75	0.57		0.78	21.92	16.44	12.49		17.10

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration* (mg/m^3)			
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin
11:28	0.87	0.66		0.90	19.33	16.82	12.76		17.40
11:31	0.90	0.67		0.94	18.70	16.83	12.53		17.58
11:34	0.90	0.64		0.93	18.70	16.83	11.97		17.39
11:37	0.91	0.65		0.93	18.70	17.02	12.16		17.39
11:40	0.90	0.66		0.92	18.70	16.83	12.34		17.20
11:43	0.95	0.68		0.98	18.70	17.77	12.72		18.33
11:46	0.95	0.70		0.93	18.70	17.77	13.09		18.33
6/4/73									
11:15	0.52	0.25		0.51	21.78	11.33	5.45		11.11
11:18	0.52	0.22		0.52	21.78	11.33	4.79		11.33
11:21	0.53	0.18		0.53	21.78	11.54	3.92		11.54
11:24	0.54	0.18		0.53	21.78	11.76	3.92		11.54
11:27	0.54	0.17		0.53	21.78	11.76	3.70		11.54
11:30	0.66	0.22		0.66	17.67	11.66	3.89		11.66
11:33	0.66	0.19		0.66	17.67	11.66	3.36		11.66
11:36	0.66	0.15		0.66	17.67	11.66	2.65		11.66
3:04	0.95	0.46		0.90	14.89	14.15	6.85		13.40
3:07	0.90	0.43		0.88	15.81	14.23	6.80		13.91
3:10	0.90	0.43		0.88	15.81	14.23	6.80		13.91
3:13	0.94	0.43		0.92	15.29	14.37	6.57		14.07
3:16	0.94	0.43		0.91	15.46	14.53	6.65		14.07
3:19	0.90	0.41		0.91	16.00	14.40	6.56		14.56
3:22	0.93	0.41		0.92	16.00	14.88	6.56		14.72
3:25	0.92	0.42		0.92	15.56	14.22	6.49		14.22
3:28	0.98	0.44		0.96	14.50	14.21	6.38		13.92
3:31	0.97	0.43		0.95	14.97	14.52	6.44		14.22
3:35	0.67	0.30		0.62	17.00	11.39	5.10		10.54
3:40	0.55	0.24		0.51	20.05	11.03	4.81		10.23
3:45	0.40	0.17		0.39	24.48	9.79	4.16		9.55
3:50	0.31	0.13		0.31	31.65	9.81	4.11		9.81
3:55	0.30	0.12		0.30	31.31	9.39	3.75		9.39
4:00	0.25	0.10		0.25	35.64	8.91	3.56		8.91

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3) Beckman	Sunshine	Dupont	Olin	Dilution Ratio	Stream Concentration* (mg/m^3) Beckman	Sunshine	Dupont	Olin
4:05	0.75	0.35		0.66	13.08	9.81	4.58		8.63
6/5/73									
2:56	0.52	0.24		0.49	16.45	8.55	3.95		8.06
3:00	0.60	0.25		0.54	15.17	9.10	3.79		8.19
3:03	0.60	0.24		0.51	16.45	9.87	3.95		8.40
3:06	0.58	0.22		0.50	17.19	9.97	3.78		8.60
3:09	0.55	0.21		0.48	18.66	10.26	3.92		8.96
3:12	0.63	0.23		0.55	16.45	10.36	3.78		9.05
3:15	0.61	0.20		0.53	16.45	10.03	3.29		8.72
3:18	0.60	0.20		0.54	17.19	10.31	3.44		9.28
3:21	0.60	0.18		0.52	17.59	10.55	3.17		9.15
3:24	0.69	0.21		0.59	15.78	10.98	3.31		9.31
3:27	0.69	0.20		0.58	17.19	11.86	3.44		9.97
3:30	0.68	0.20		0.58	17.19	11.69	3.44		9.97
4:08	0.90	0.37		0.74	13.50	12.15	5.00		9.99
4:11	0.95	0.38		0.80	13.50	12.83	5.13		10.80
4:14	0.98	0.39		0.80	13.27	13.00	5.18		10.62
4:17	1.00	0.40		0.82	13.05	13.05	5.22		10.70
4:20	0.89	0.36		0.71	13.88	12.35	5.00		9.85
4:23	0.87	0.36		0.73	13.88	12.08	5.00		10.13
4:26	0.90	0.38		0.74	13.88	12.49	5.27		10.27
4:29	0.90	0.38		0.72	14.40	12.96	5.47		10.37
4:32	0.90	0.38		0.72	14.40	12.96	5.47		10.37
4:35	0.85	0.36		0.70	14.96	12.72	5.39		10.47
4:38	0.87	0.36		0.71	14.96	13.02	5.39		10.62
6/6/73									
9:05	0.60	0.37		0.66	18.37	11.02	6.80		12.12
9:10	0.95	0.49		0.92	17.25	16.39	8.45		17.25
9:13	0.80	0.41		0.89	18.57	14.86	7.61		18.01
9:16	0.80	0.39		0.88	18.57	14.86	7.24		17.83
9:19	0.85	0.39		0.85	20.51	17.43	8.00		19.07
9:22	0.76	0.32		0.85	19.18	14.58	6.14		17.84
9:25	0.73	0.28		0.82	20.51	14.97	5.74		18.46

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3) Beckman	Sunshine	Dupont	Olin	Dilution Ratio	Stream Concentration* (mg/m^3) Beckman	Sunshine	Dupont	Olin
9:28	0.73	0.26		0.81	20.05	14.64	5.21		17.84
9:31	0.71	0.22		0.81	20.51	14.56	4.51		18.25
9:34	0.71	0.19		0.81	20.51	14.56	3.90		18.25
9:37	0.70	0.17		0.81	21.00	14.70	3.57		18.69
9:40	0.70	0.17		0.81	21.00	14.70	3.57		18.69
10:10	0.85	0.52		0.90	16.09	14.45	8.84		15.30
10:15	0.84	0.49		0.87	16.38	13.76	8.03		14.25
10:20	0.85	0.49		0.85	17.00	14.45	8.33		14.45
10:23	0.85	0.48		0.90	17.33	14.73	8.32		15.60
10:26	0.82	0.47		0.85	18.39	15.08	8.64		15.63
10:29	0.83	0.48		0.88	17.00	14.11	8.16		14.96
10:32	0.83	0.48		0.86	17.67	14.67	8.48		15.20
10:35	0.81	0.47		0.85	17.67	14.31	8.30		15.02
10:38	0.82	0.48		0.86	20.05	16.44	9.62		17.24
10:41	0.84	0.48		0.87	18.39	15.45	8.83		16.00
10:44	0.84	0.49		0.88	17.00	14.28	8.33		14.96
10:47	0.82	0.47		0.84	17.67	14.49	8.30		14.84
10:50	0.81	0.47		0.85	19.18	15.54	9.01		16.30
10:55	0.81	0.46		0.83	17.00	13.77	7.82		14.11
11:00	0.85	0.47		0.83	16.38	13.92	7.70		13.60
11:05	0.85	0.46		0.82	16.38	13.92	7.53		13.43
11:10	0.85	0.46		0.84	16.38	13.92	7.53		13.76
11:15	0.84	0.46		0.82	16.38	13.76	7.53		13.43
11:20	0.85	0.46		0.82	16.38	13.92	7.53		13.43
11:23	0.85	0.46		0.91	16.38	13.92	7.53		14.91
11:26	0.80	0.45		0.85	14.79	11.83	6.66		12.57
11:29	0.85	0.47		0.92	15.81	13.44	7.43		14.55
11:32	0.85	0.45		0.93	16.09	14.37	7.61		15.72
11:35	0.85	0.45		0.93	15.81	13.44	7.11		14.70
11:38	0.85	0.44		0.93	15.81	13.44	6.96		14.70
11:41	0.85	0.44		0.94	15.81	13.44	6.96		14.86
11:44	0.85	0.43		0.95	15.55	13.22	6.69		14.77
11:47	0.86	0.44		0.96	15.81	13.60	6.96		15.18
11:50	0.87	0.44		0.97	14.79	12.87	6.51		14.35

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration* (mg/m^3)			
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin
1:30	0.60	0.33		0.59	18.86	11.31	6.22		11.13
1:33	0.72	0.41		0.69	17.20	12.38	7.05		11.87
1:36	0.70	0.40		0.67	17.20	12.04	6.88		11.52
1:39	0.68	0.39		0.65	18.74	12.74	7.31		12.18
1:42	0.65	0.36		0.63	19.63	12.76	7.07		12.37
1:45	0.80	0.44		0.77	16.20	12.96	7.13		12.47
1:48	0.90	0.50		0.90	13.93	12.54	6.97		12.54
1:51	0.89	0.49		0.88	13.93	12.40	6.83		12.26
1:54	0.89	0.48		0.88	14.16	12.60	6.80		12.46
1:57	0.87	0.48		0.88	13.93	12.12	6.69		12.26
2:00	0.85	0.47		0.87	13.93	11.85	6.55		12.12
2:05	0.83	0.46		0.87	14.89	12.36	6.85		12.95
2:08	0.83	0.45		0.89	14.89	12.36	6.70		13.25
2:11	0.82	0.45		0.88	14.89	12.21	6.70		13.10
2:14	0.84	0.46		0.90	14.39	12.09	6.62		12.95
2:17	0.80	0.44		0.87	15.15	12.12	6.67		13.18
2:20	0.81	0.45		0.88	15.15	12.27	6.82		13.33
2:23	1.00	0.52		1.00	13.50	13.50	7.88		13.50
2:26	0.92	0.51		0.98	10.80	9.94	5.51		10.58
2:30	0.80	0.43		0.84	13.14	10.51	5.65		11.04
2:55	0.81	0.46		0.79	17.67	14.31	8.13		13.96
2:58	0.67	0.35		0.68	19.18	12.85	6.71		13.04
3:01	0.83	0.45		0.83	18.78	15.59	8.45		15.59
3:04	0.93	0.50		0.92	17.00	15.81	8.50		15.64
3:07	0.87	0.48		0.84	17.67	15.37	8.48		14.84
3:10	0.78	0.42		0.74	19.18	14.96	8.06		14.19
3:13	0.82	0.47		0.79	17.00	13.94	7.99		13.43
3:16	0.78	0.46		0.73	18.39	14.34	8.46		13.42
3:19	0.77	0.44		0.73	18.39	14.16	8.09		13.42
3:22	0.75	0.44		0.70	18.39	13.79	8.09		12.87
3:25	0.77	0.44		0.73	18.39	14.16	8.09		13.42
3:35	0.65	0.42		0.68	22.62	14.70	9.50		15.38
3:38	0.63	0.39		0.66	22.62	14.25	8.82		14.92
3:41	0.57	0.36		0.61	25.24	14.39	9.09		15.40

TABLE 4-5 (CONTINUED)

Date-Time	Instrument Readings (mg/m^3)				Dilution Ratio	Stream Concentration* (mg/m^3)			
	Beckman	Sunshine	Dupont	Olin		Beckman	Sunshine	Dupont	Olin
3:44	0.58	0.37		0.62	24.19	14.03	8.95		15.00
3:47	0.61	0.39		0.66	23.22	14.16	9.06		15.33
3:50	0.60	0.38		0.62	24.19	14.51	9.19		15.00
3:53	0.52	0.34		0.57	25.24	13.12	8.58		14.36
3:56	0.45	0.28		0.48	28.59	12.73	7.92		13.58
3:59	0.44	0.28		0.49	29.27	12.88	8.20		14.34
4:02	0.45	0.27		0.48	28.59	12.87	7.72		13.72
4:05	0.42	0.26		0.46	30.63	12.86	7.96		14.09

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* Instrument readings multiplied by dilution ratio.

TABLE 4-6

HYDROGEN STREAM SAMPLES

	Date	Type	Hg Conc by AA Analysis (mg/m^3)	Beckman mg/m^3	Olin mg/m^3	Sunshine mg/m^3
1.)	5/31	ICL	0.94	0.74	0.74	0.62
2.)	5/31	ICL	0.95	0.78	0.81	0.46
3.)	5/31*	ICL	1.08	0.65	0.71	0.44
4.)	5/31*	$KMNO_4$	1.25	0.65	0.71	0.44
5.)	5/31	ICL	1.28	0.80	0.77	0.46
6.)	6/1	ICL	1.06	0.79	0.73	0.59
7.)	6/1	$KMNO_4$	0.85	0.85	0.88	0.63
8.)	6/4*	ICL	1.33	0.93	0.92	0.43
9.)	6/4*	$KMNO_4$	1.22	0.93	0.92	0.43
10.)	6/5	ICL	0.94	0.62	0.54	0.21
11.)	6/5	ICL	1.28	0.91	0.81	0.37
12.)	6/6*	ICL	1.07	0.77	0.84	0.30
13.)	6/6*	$KMNO_4$	0.75	0.77	0.84	0.30
14.)	6/6*	ICL	1.23	0.83	0.86	0.48
15.)	6/6*	$KMNO_4$	0.86	0.83	0.86	0.48
16.)	6/6	$KMNO_4$	0.84	0.85	0.92	0.42

* Simultaneous Tests

TABLE 4-6

HYDROGEN STREAM SAMPLES

	Date	Type	Hg Conc by AA Analysis (mg/m^3)	Beckman mg/m^3	Olin mg/m^3	Sunshine mg/m^3
17.)	6/6	$KMNO_4$	0.70	0.77	0.76	0.43
18.)	6/6	$KMNO_4$	0.68	0.70	0.74	0.42
19.)	6/6	$KMNO_4$	0.60	0.80	0.77	0.45
20.)	6/6	$KMNO_4$	0.53	0.53	0.58	0.34

APPENDIX B

STATE-OF-THE-ART REPORT ON EVALUATION OF INSTRUMENTATION FOR MONITORING TOTAL MERCURY EMISSIONS FROM STATIONARY SOURCES

I. INTRODUCTION

This report reviews the physical and chemical principles for the continuous monitoring of mercury. Although UV absorption has been the most popular technique for monitoring mercury, many different configurations have been employed, e.g., single beam, dual beam, dual wavelength. The advantages and disadvantages of each technique are discussed in Section 2.

Mercury can be present in several different forms, namely elemental mercury, inorganic compounds ($HgCl_2$, HgO, etc.) and organic compounds [$Hg(CH_3)_2$]. Since all the commercially available mercury detectors sense only elemental mercury, inorganic and organic mercury compounds must be decomposed in order to have a system which is capable of monitoring total mercury emissions. In Section 3, the requirements for sampling mercury in different stationary sources are covered.

Section 4 describes the characteristics of a number of commercially available mercury monitors and evaluates their use as either continuous-inplace monitors or portable monitors for compliance testing.

II. PRINCIPLES OF DETECTION

A. ULTRAVIOLET ABSORBANCE

Optical instrumentation has been the most universal approach for mercury analysis and monitoring. These optical techniques utilize the strong ultraviolet absorbance of mercury vapor at 253.7 nm. Since mercury is an atomic species, it absorbes and emits energy of the same frequency. This phenomenon is termed resonance radiation. Thus, a high voltage or high frequency discharge containing mercury in the presence of an inert gas will emit radiation which will be absorbed by mercury vapor. If the pressure of the discharge is low, the mercury will emit 85-95% of its energy at the 253.7 nm resonance line.

The extinction coefficients for mercury and a number of other species [1,2] are given in Table 2-1. The list contains only a few of many compounds which absorb at 253.7 nm. The technique is clearly not specific for mercury, but its strong absorption allows mercury to be determined in the presence of 100-1000 times the concentration of weakly absorbing species. This is not enough, however, for sources which emit mercury in low concentrations in the presence of high levels of sulfur dioxide.

UV analyzers are commercially available in a variety of configurations including single beam, dual wavelength and dual beam. Several approaches have been used to increase the rejection ratio for interferences and make the instruments more specific for mercury. One approach uses Zeeman splitting of the mercury resonance line while another makes use of the pressure broadening of the 253.7 nm mercury line. A third approach to imporve the specificity involves the isolation of mercury by absorption on a noble metal (silver or gold) collector and subsequent thermal desorption and analysis.

TABLE 2-1

COMPARISON OF SOME ULTRAVIOLET ABSORBING SPECIES AT 253.7 NM

Species	Approximate Extinction Coefficient (1/mole-cm) at 253.7 nm	Rejection Ratio*
mercury	4×10^6	
sulfur dioxide	40	10^4
hydrogen sulfide	2	2×10^5
ozone	3000	133
dinitrogen tetroxide (N_2O_4)	200	2×10^3
benzene	200	2×10^3
chlorine	1	4×10^5
nitrogen dioxide	10	4×10^4

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* defined as the concentration ratio which will produce less than a 10% error in the mercury concentration

The various techniques are described in the following sections.

1. Single Beam UV

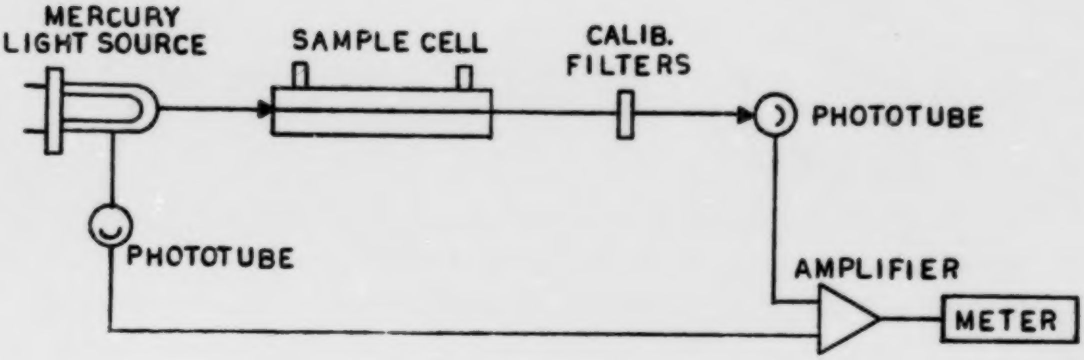
A single beam UV monitor consists of a low pressure mercury light source, a sample cell, phototube and amplifier. A typical block diagram is shown in Figure 2-1(a). Most of these instruments have a dual phototube arrangement. One phototube (a) is placed adjacent to the light source and measures the intensity of the source (I_0). The other phototube (b) measures the attenuation of the light source (I) by mercury in the sample cell. These instruments measure the ratio of I/I_0 which is related to the concentration. In some instruments, a nonlinear (logarithmic) scale is provided, while others utilize logarithmic amplifiers to perform a subtraction of $I - I_0$ and have a linear output.

2. Dual Wavelength

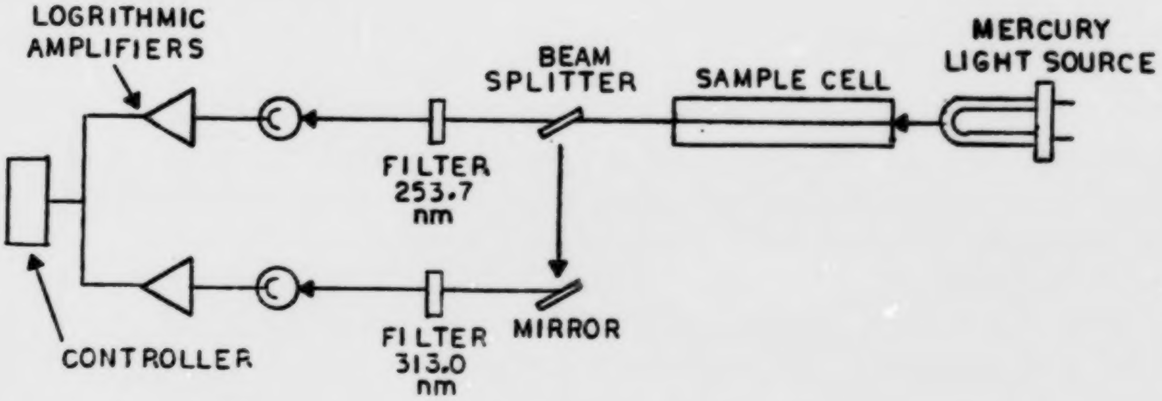
This is similar to the single beam system except that two different wavelengths are used. In dual wavelength-single cell systems, the unfiltered radiation from a low pressure mercury discharge passes through the sample cell and then is split into two beams by a half-silvered mirror. The radiation in each beam is then isolated into two discrete wavelengths by a 253.7 nm or a 313 nm interference filter respectively. The later wavelength where mercury does not absorb is used as a reference signal for comparison to 253.7 nm where mercury absorbes strongly.

The intensities of the absorbing and reference wavelengths are measured with phototubes coupled to logarithmic amplifiers. Subtraction of the 253.7 nm signal from the 313 nm value provides an output which increases linearly with mercury concentration. A schematic of this system is given in Figure 2-1(b).

Another version of this instrument employs two interference filters mounted on a rotating plate and a single phototube detector.


MERCURY LIGHT SOURCE
SAMPLE CELL
CALIB. FILTERS
PHOTOTUBE
PHOTOTUBE
AMPLIFIER
METER

(a) SINGLE BEAM SYSTEM


LOGRITHMIC AMPLIFIERS
BEAM SPLITTER
SAMPLE CELL
MERCURY LIGHT SOURCE
FILTER 253.7 nm
CONTROLLER
FILTER 313.0 nm
MIRROR

(b) DUAL WAVELENGTH SYSTEM

Figure 2-1. Single beam and Dual Wavelength UV Analyzers

The advantages of the single cell-dual wavelength approach include compensation for: a) the aging of the lamp; b) the buildup of dust or deposits on the cell windows; and c) the presence of particulate matter in the sample stream. This system will also compensate for UV absorbing gases which have the same absorbances at the two wavelengths. Corte and Dubois [3] have demonstrated, however, that organics, sulfur dioxide, and many other interfering species may not be adequately compensated for with this approach.

Another version of the dual wavelength approach involves splitting the beam before it is passed through the sample. A separate cell is used for the reference wavelength. This approach does not offer any advantage for mercury monitoring over the two techniques described above. In fact, it is less favorable in that buildup of particulate on the cell windows and particulate matter in the gas stream is not compensated for.

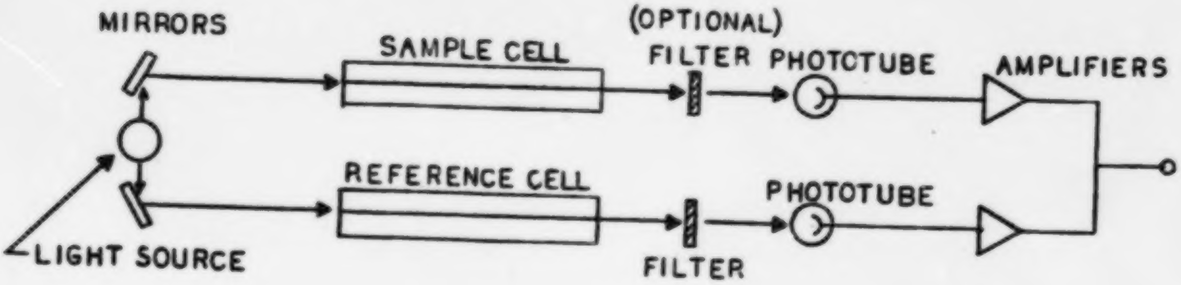
Although some of the differences between the instruments appear slight, these simple modifications may influence the results obtained.

Many of these dual wavelength instruments are very expensive and not very portable.

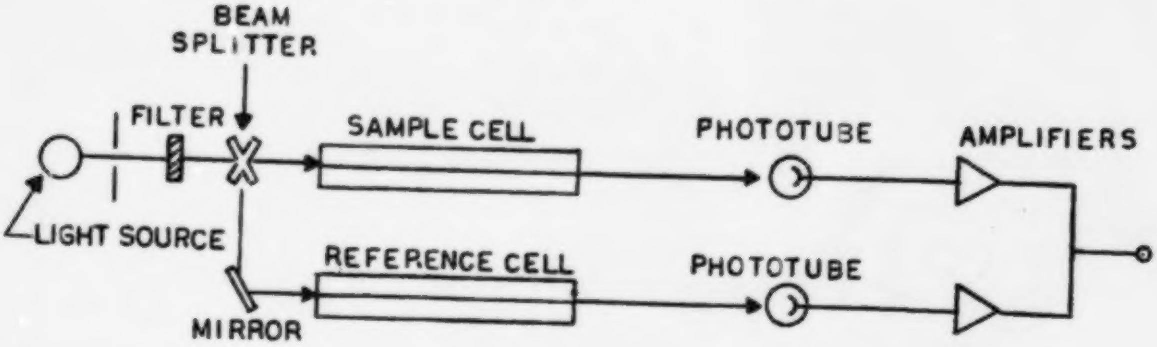
3. Dual Beam

A dual beam system, in the usual sense, refers to comparison of intensity measurements in a sample cell and reference cell where light of the same frequency is passed through both cells. Two schematics of possible dual beam systems are shown in Figure 2-2 (a and b).

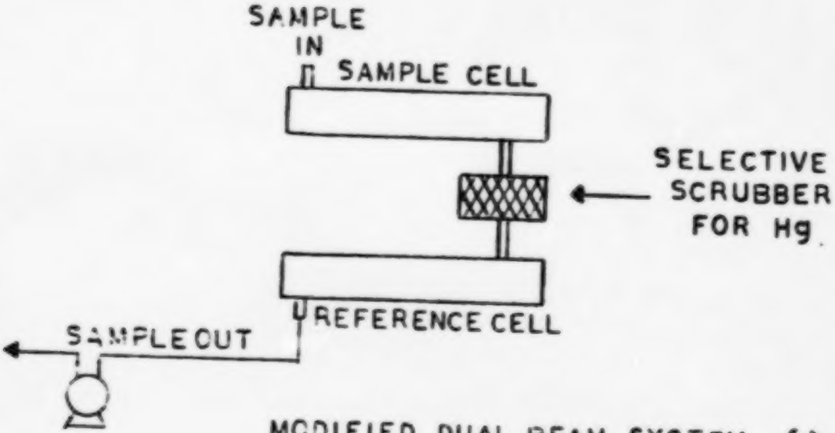
The dual beam system, as normally used, does not offer any advantage over the single beam system. Corte and Dubois [3] have investigated methods for improving the specificity of mercury analyzers. Their approach involves the use of a modified dual-beam system where a mercury


MIRRORS
SAMPLE CELL
(OPTIONAL)
FILTER
PHOTOTUBE
AMPLIFIERS
REFERENCE CELL
PHOTOTUBE
LIGHT SOURCE
FILTER

DUAL BEAM SYSTEM (a)


BEAM
SPLITTER
FILTER
SAMPLE CELL
PHOTOTUBE
AMPLIFIERS
LIGHT SOURCE
REFERENCE CELL
PHOTOTUBE
MIRROR

DUAL BEAM SYSTEM (b)


SAMPLE
IN
SAMPLE CELL
SELECTIVE
SCRUBBER
FOR Hg
REFERENCE CELL
SAMPLE OUT

MODIFIED DUAL BEAM SYSTEM (c)

Figure 2-2. Dual Beam UV Mercury Analyzers

scrubber is placed in series with the sample cell. The sample then flows through the sample cell, the mercury scrubber, and into the reference cell. A schematic of the system is given in Figure 2-2(c). The advantage of this system is that if only mercury is removed in the scrubber the difference between the sample cell and reference cell represents the absorption due to mercury and a truly mercury specific analyzer is available. Corte and Dubois [3] found that either palladium chloride or silver wool filters effectively removed mercury while quantitatively passing organics and fine particulate matter. Although granulated zinc and charcoal absorb mercury, the former absorbent melts when heated to release the mercury, and the latter compound also absorbs organics, sulfur dioxide, etc..

Corte and Dubois [3] conclude that only a "true double beam" UV instrument with a mercury scrubber is satisfacotry for obtaining a signal which is specified for mercury in air.

4. Zeeman Effect

In a strong magnetic field, the resonance line of mercury (253.7 nm) is split into three components σ^+, σ^- and π. The frequencies of these three Zeeman components can be defined by [4].

$$v(\sigma^+) = Vo + \delta v$$
$$v(\pi) = Vo$$
$$v(\sigma^-) = Vo - \delta v$$

where Vo is the frequency of mercury and δv is the frequency shift due to the Zeeman effect. As the strength of the magnetic field increases, δv increases linearly and only the π component lies within the absorption profile [4] in a strong magnetic field [see Figure 2 in Reference 4]. Several different schemes utilizing this concept have been demonstrated.

One is described in detail by Hadeishi and McLaughlin [4]. The radiation from an electroeless mercury discharge lamp* placed in a magnetic field passes first through the absorption cell, then through 253.7 nm filter, and to a beam splitter. The beam perpendicular to the optical path passes directly to a phototube and amplifier. The other beam passes through a cell filled with mercury vapor then to a phototube and associated amplifier. A schematic of the system is shown in Figure 2-3. Since the magnetic field is on continuously, phototube (a) perpendicular to the optical path measures the σ^+ and σ^-, and π components. The other phototube (b) measures only the σ^+ and σ^- components since the π component (but not the σ components) would be absorbed by the mercury vapor. The difference between these two signals provide a response which is specific for mercury.

Another system which is similar in principle to that of Hadeishi and McLaughlin yet different in design is commercially available from Scintrex. This instrument is bulky, and employs a Hg^{201} discharge lamp with a large magnet (high magnetic fields). Since the instrument was designed to measure mercury in the ambient air (ng/m^3 region), an optical path length of about 30 ft is employed. The dual beam system uses a pulsed magnetic field and measures the difference in absorption with the magnetic field pulsed on and off with a phase sensitive amplifier. The reference signal (zero) is obtained by passing the sample through a palladium chloride coated filter to remove mercury. The selectivity ratio for Hg/SO_2 is 500,000:1. When this is compared with the rejection ratio for UV absorbance (Table 2-1), the advantages of this instrument become quite apparent.

5. Pressure Broadening

Other approaches for increasing the specificity of UV absorption for mercury utilize the pressure broadening of atomic emission lines (@253.7 nm) from mercury discharges.

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* The HG^{199} isotope lamp was used to reduce the strength of the magnetic field required, and hence the weight of the magnet.

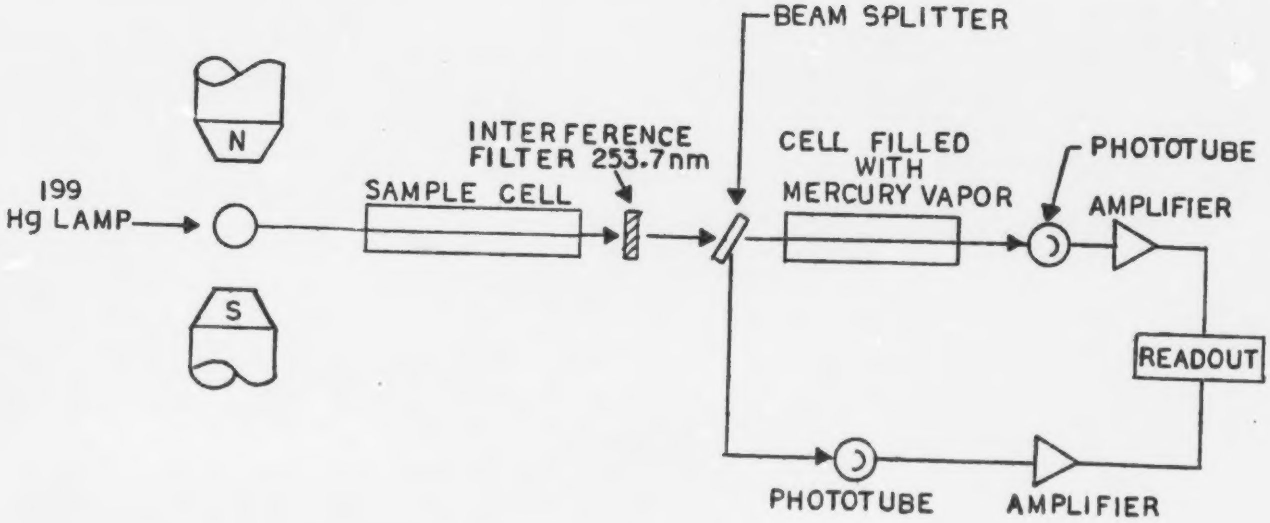

BEAM SPLITTER
N
INTERFERENCE FILTER 253.7nm
CELL FILLED WITH MERCURY VAPOR
PHOTOTUBE
199 Hg LAMP
SAMPLE CELL
AMPLIFIER
S
READOUT
PHOTOTUBE
AMPLIFIER

Figure 2-3. Zeeman Effect Mercury Meter

A schematic of Barringer's [5] mercury monitor is shown in Figure 2-4. The output from the low pressure mercury lamp passes sequentially through the sample, a 253.7 nm interference filter, then is split into two components. One beam is deflected onto a phototube (a) while the other passes through a cell filled with mercury vapor prior to measurement by another phototube (b). The output of the lamp is slightly broadened and passage of the beam through the mercury vapor cell causes complete absorption of only the center of the broadened 253.7 nm line. This phototube then does not respond to mercury addition to the sample cell but will respond to species which absorb at the edges of broadened 253.7 nm line. The other phototube (a) is very sensitive to mercury. The output of these two photobubes is coupled to a differential amplifier. If a boradened UV absorber, e.g., an organic species, is placed in the sample cell, this will result in a reduction in intensity in both phototubes and record a net change of zero. The rejection of interferences for this instrument is demonstrated in Table 2-2 below:

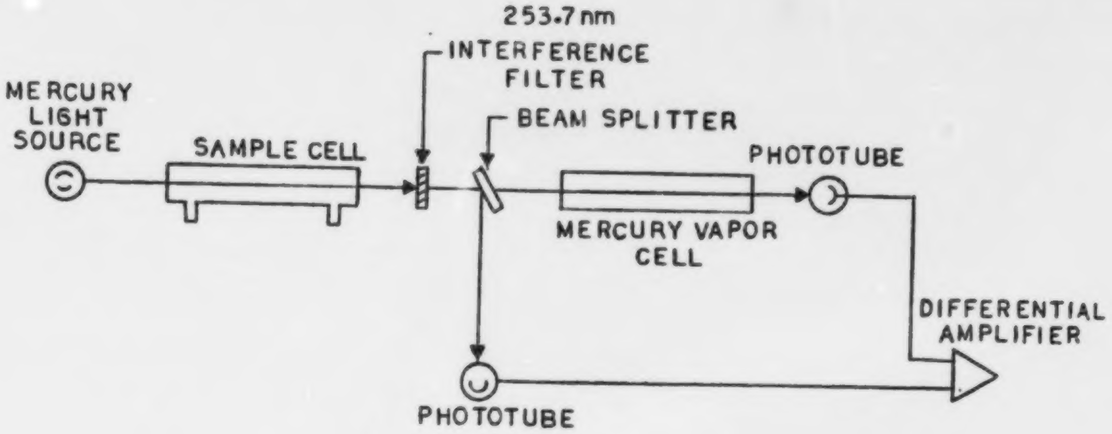
TABLE 2-2

Rejection of Interferences for Barringer Spectrometer

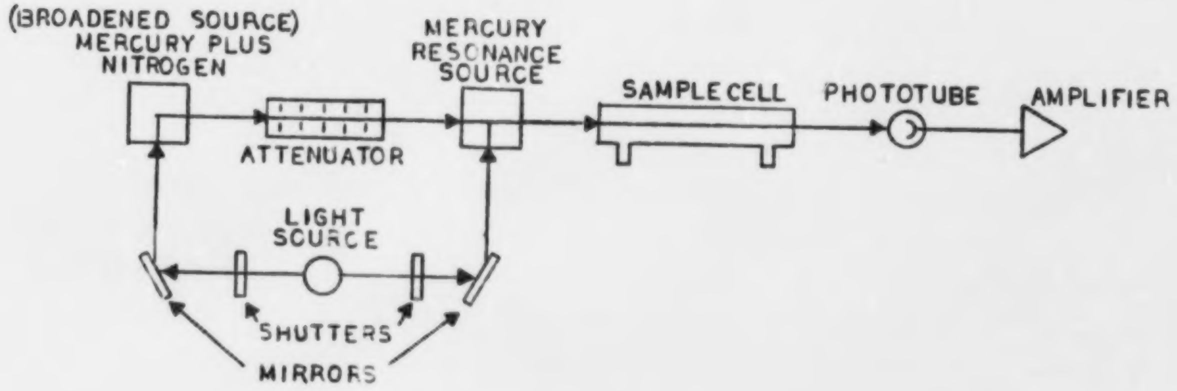
Compound	Rejection Ratio
Benzene	$1:2 \times 10^5$
Toluene	$1:2 \times 10^5$
Cyclohexene	$1:2 \times 10^6$
Dioxane	$1:1 \times 10^6$
Carbon Dioxide	$1:2 \times 10^6$

These data can be compared with benzene rejection for a simple UV absorption system in Table 2-1. The improvement in specificity is quite impressive.

Ling [6,7] described an instrument of different configuration which used essentially the same principle. His instrument is shown in Figure 2-4. Ling [6] irradiated the sample alternately with a pressure


253.7 nm
INTERFERENCE FILTER
MERCURY LIGHT SOURCE
SAMPLE CELL
BEAM SPLITTER
PHOTOTUBE
MERCURY VAPOR CELL
DIFFERENTIAL AMPLIFIER
PHOTOTUBE

(a) AFTER BARRINGER


(BROADENED SOURCE) MERCURY PLUS NITROGEN
ATTENUATOR
MERCURY RESONANCE SOURCE
SAMPLE CELL
PHOTOTUBE
AMPLIFIER
LIGHT SOURCE
SHUTTERS
MIRRORS

(b) AFTER LING

Figure 2-4. Mercury Analyzers Depending on Pressure Broadening Effects

broadened mercury source (mercury plus nitrogen) and a high vacuum mercury resonance lamp. The difference in absorbance obtained between these two lamps provides a signal which is specific for mercury. When mercury vapor is added to the sample cell, 99% of the radiation from the mercury resonance line is absorbed whereas only 2% of the intensity from the pressure broadened source is absorbed.

Neither of these instruments is commercially available on a regular basis although several prototypes of the Barringer instrument have been used in prospecting.

6. Amalgamation

Mercury forms amalgams with a number of noble metals including gold and silver. Williston [8] and Long et.al. [9] have utilized silver wool for collection of mercury in ambient air. Tradet [10] developed a procedure for collection of mercury in the presence of high concentrations of SO_2 by amalgamation on gold or silver to concentrate the mercury in the sample and pass interferences such as sulfur dioxide and hydrocarbons. These instruments are batchtype analyzers in that mercury is collected by amalgamation for a known period of time at a constant flow, then the mercury is desorbed by heating. Two of the commercial analyzers employing this principle are of the single beam UV type while one employes condensation nuclei formation for mercury detection. The difficulties are the dependence on flow rate, the low collection efficiency for mercury on the commercial type amalgamators, and the effect which corrosive materials (H_2SO_4, Cl_2, etc.) have on the surface characteristics of the amalgamators. This latter feature also leads to low recoveries of mercury.

B. SELENIUM SULFIDE

Elemental mercury reacts with selenium sulfide to produce the black precipitate mercuric sulfide. Paper coated with selenium sulfide has been used to detect mercury [11]. The instrument normally used for this application is the tape stain sampler where a decrease in the % of the paper due to the formation of HgS is directly proportional to the mercury concentration. No continuous monitors utilizing this principle are commercially available. Considerable modifications to commercial tape stain samplers would be required to obtain a continuous monitor. In addition, this technique requires the temperature to be maintained constant, and the paper to be shielded from strong light. The useful life of the paper is of the order of six months to one year as a result of aging.

C. CONDENSATION NUCLEI

When elemental mercury, in the presence of oxygen is irradiated with ultraviolet light, fine particles of mercuric oxide are formed. These nuclei are drawn into a chamber where an expansion at constant volume produces an opaque cloud. A light scattering photometer is then used for determining the transmission which is related to the concentration.

Particulate matter must be very efficiently removed to prevent an interference. This could result in losses of mercury vapor by absorption on the filter. Some problems may be observed as a result of the requirement to produce particles of uniform size.

III. SAMPLING REQUIREMENTS FOR STATIONARY SOURCES

The principal industrial sources of mercury emitted to the atmosphere include:

--chlor-alkali
--primary mercury production
--secondary mercury processing
--non-ferrous smelting
--coal burning power plants
--incinerators

Each of these sources will have its own characteristic problems with sampling. For example, the chlor-alkali and mercury smelting processes have high mercury levels which may require the use of a short path cell and/or possibly sample dilution. Particulate mercury compounds such as $HgCl_2$ or HgO are also present which require a catalytic converter to decompose them to elemental mercury. The latter source has high concentrations of SO_2 which may require a scrubber for most types of analyzers. The non-ferrous smelters and coal-fired power plants are typified by high levels of SO_2 and relatively low levels of mercury. Most commercial mercury monitors will require a scrubber to remove SO_2. A summary of mercury concentrations for some stationary sources is given in Table 3-1.

The sampling conditioning requirements for the different types of mercury analyzers is given in Table 3-2. Note that all the mercury analyzers, regardless of the principle of detection, require a pyrolyzer or catalytic converter to reduce particulate mercury compounds to mercury vapor. An additional feature of the pyrolyzer is that all hydrocarbons are combusted to CO_2, thereby eliminating the hydrocarbon interference noted for the UV absorption analyzers in Table 3-2. Commercially available pyrolyzers usually operate at about 600°C to decompose organic and inorganic (particulate) mercury compounds [12, 13, 14] but they are capable of operation at temperatures as high as 800°C.

TABLE 3-1

SUMMARY OF EPA MERCURY EMISSIONS DATA

SUMMARY OF EPA MERCURY EMISSIONS DATA

Type of Plant	Site	Range of Total Hg Conc.
Chlor-alkali (Wynd.)	H_2 Stack	$40\text{-}1.6 \times 10^3$ mg/m^3
Chlor-alkali (B.F.G.)	H_2 Stack	2.5-10 mg/m^3
	Fume System	4-12 mg/m^3
	Cell Room	$3 \times 10^{-3}\text{-}5 \times .0^{-3}$ mg/m^3
Chlor-alkali (D.S.)	H_2 Stack	1-3 mg/m^3
	End Box Vent	$1 \times 10^3\text{-}2.5 \times 10^3$ mg/m^3
Chlor-alkali (G.P.)	Vent System (end room)	2.7×10^3 mg/m^3
	H_2 Stack	$2 \times 10^2\text{-}4 \times 10^2$ mg/m^3
Coal-Fired P.P.		0.1 mg/m^3
Mercury Smelter (El Paso Gas)	Stack	$1 \times 10^2\text{-}6 \times 10^2$ mg/m^3
Hg Smelter (N.I.)	Stack	$9 \times 10^2\text{-}11 \times 10^2$ mg/m^3
Hg Smelter (Sonoma)	Stack	~ 1.3 mg/m^3

TABLE 3-2

SAMPLE CONDITIONING REQUIREMENTS FOR DIFFERENT TYPES OF MERCURY ANALYZERS

Principle	Manufacturer	Isokinetic Sampling	Hydrocarbon Removal	SO_2 Removal	Pyrolyzer to Convert Particulate to Elemental Mercury
UV Absorption	Sunshine Beckman Olin Dupont Geomet	Yes	Yes	Yes	Yes
Pressure Broadening	Barringer	Yes	No	No	Yes
Zeeman Effect	Sintrex	Yes	No	No	Yes
Condensation Nuclei	Environment One	Yes	?	?	Yes
Tape Stain*	RAC Sunshine Scien.	Yes	No	No	Yes

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*Particulate matter must be very efficiently removed, otherwise it will also result in a decrease in transmission.

For those sources which contain high levels of SO_2 an aqueous sodium carbonate scrubber has shown to remove SO_2 but quantitatively pass elemental mercury [15].

A compilation of the sample conditioning requirements for the different industrial processes is given in Table 3-3. An additional sampling requirement which may be necessary is the use of isokinetic sampling for sources which contain particulate mercury.

TABLE 3-3

SAMPLE CONDITIONING REQUIREMENTS FOR DIFFERENT PROCESSES

Source	Elemental Mercury	Particulate Mercury	Organic Mercury	SO_2	Hydrocarbons	Requirements
Chloralkali	Yes	Yes ($HgCl_2$, HgO)	No	No	No	(a) Isokinetic sampling (b) Pyrolyzer to decompose inorganic mercury compounds
Hg Smelter	Yes	Yes (HgO)	No	Yes	Yes	(a) SO_2 removal necessary only for low Hg emissions (b) HC removal (?) (c) Isokinetic sampling (?)
Non-ferrous Smelter	Yes	No	No	Yes	Yes	(a) SO_2 removal
Secondary Hg Processing	Yes	No	Yes	No	Yes	(a) Conversion of organic Hg to elemental Hg
Incinerator	Yes	Possibly (b)	?	--	Yes	(a) Hydrocarbon removal (b) Possibly particulate Hg where large quantities of PVC are incinerated
Coal-Fired Power Plant	Yes	No	No	Yes	Yes	(a) SO_2 removal (b) HC removal in the case of poor combustion

IV COMMERCIALLY AVAILABLE MERCURY MONITORS

Commercially available mercury monitors can be divided into portable instruments and continuous-in-place monitors. The former instruments are most useful for compliance testing because of their light weight, e.g. about 50 lbs. or less. Many of the instruments, however, can be used for both categories. The portable monitors are not expected to be exceptionally stable with regard to zero and span while the continuous-in-place monitors are expected to have better stability characteristics. None of the instruments, as sold, have sampling systems which are adequate for monitoring total mercury emissions from the sources listed in Section III. The Olin monitor has both a catalytic converter and an acidic $SnCl_2$ scrubber. Both of these are located in the instrument and could lead to serious loss of particulate mercury compounds, especially if long sampling lines are utilized. The characteristics of some commercially available portable and continuous-in-place monitors are given in Tables 4-1 and 4-2 respectively. The approximate prices in the tables are for the analyzer alone unless otherwise noted.

TABLE 4-1

PORTABLE MERCURY MONITORS

Manufacturer	Principle	Concentration Range	Approximate Price	Weight (lbs)	Remarks
Beckman (K23)	Single beam UV-dual detector	0-1 mg/m^3	\$890 \$240	7	has built in calibrator; optional cell required for use as an extractive sampler
Sunshine Scientific (38E)	Single beam UV-dual detector	0-0.3 mg/m^3	\$1500	8	must be modified before use
Geomet (103-4)	Amalgamation	ng/m^3 - mg/m^3	\$7600	35	mercury preconcentrated in gold or silver gridbatch type operation
Bacharach ( )	Amalgamation - single beam UV	0-1 mg/m^3	\$1900	20	Gold collection matrix and internal combustion furnac
Environment/ One	Amalgamation - Condensation Nuclei	0.01-1 µg/m^3	\$5800	54	Silver wool collector
L.D.C.	Dual beam UV	0-0.25 µg/m^3	\$1800	25	30 cm absorption cell used mainly for ambient air
Mercometer	Dual beam-UV	10 µg/m^3 → up	\$1200	27	

TABLE 4-2

CONTINUOUS-IN-PLACE MERCURY MONITORS

Manufacturer	Principle	Concentration Range	Approximate Price	Weight (lbs)	Remarks
DuPont (400)	Dual wavelength UV	0.1-2000 μg/m^3	\$5000	130	
Olin	Dual wavelength UV	0-2 ng/m^3 or higher	\$19,000	800	Has $SnCl_2$ scrubber, pyrolyze and multipoint sampling capability
Geomet (103-4)	Amalgamation-single beam UV	10 ng/m^3 → up	\$7600	35	(see previous table)
Scintrex	UV absorption-Zeeman effect	0-2.5 μg/m^3	\$17,300	100	Designed mainly for ambient air but would be useful for stacks with a shorter cell
Teledyne	Dual wavelength-UV; single beam UV	0-8000 μg/m^3	\$5800 \$4400	100	
Environment/One	Amalgamation-condensation nuclei	0.01-1 μg/m^3	\$5800		Silver wool collection

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